THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVIII | MAY 1953 | No. 5

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Secretary's Note - - -

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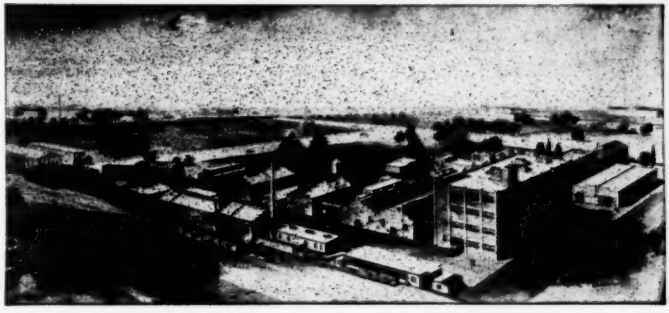

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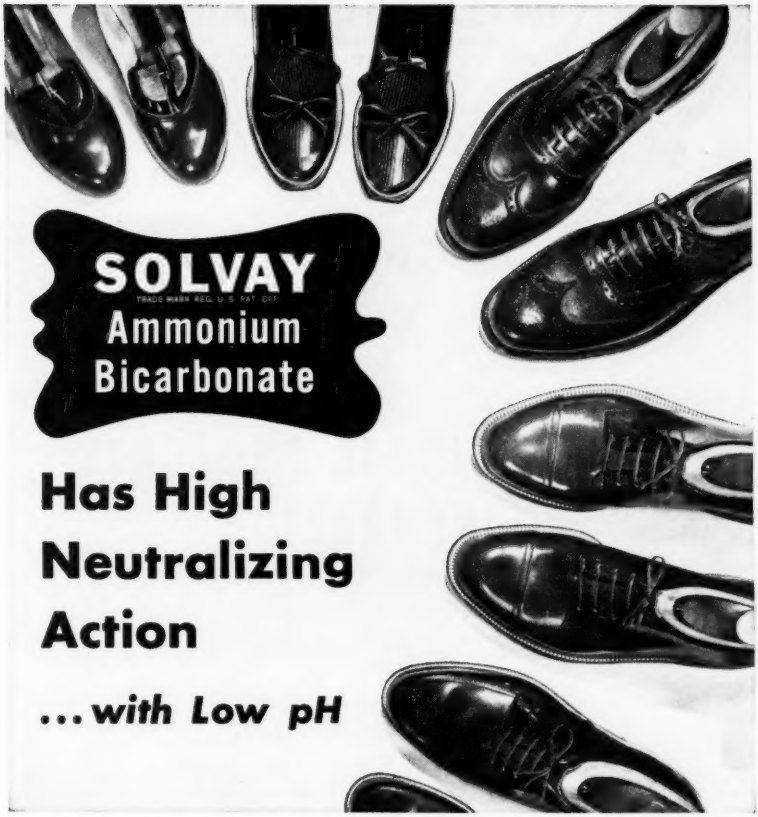

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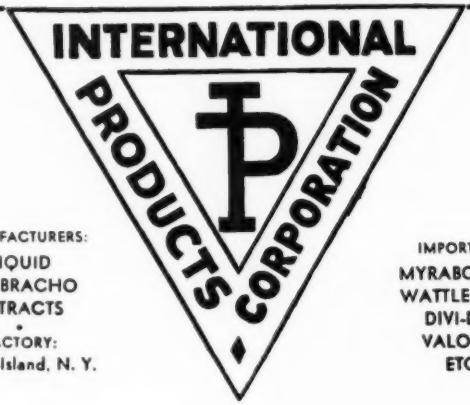

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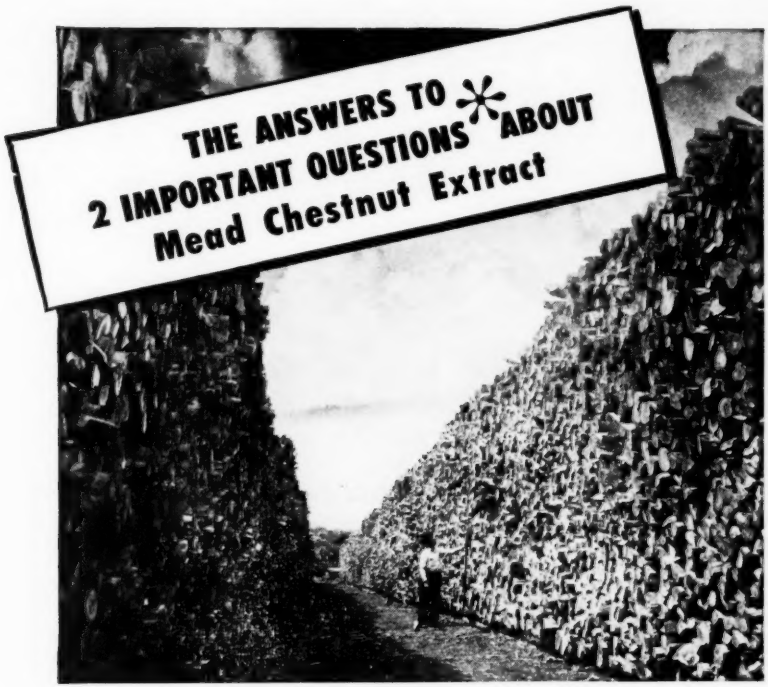

This is only a portion of the many stockpiles of chestnut logs that insure a continuous supply of Chestnut Extract.

1. Is the supply of Mead Chestnut Extract adequate?

Decidedly yes. Recent surveys show that there is enough chestnut wood in our forests to serve the leather industry for many years to come. Huge chestnut stockpiles, such as the one shown above, are converted under chemical control at five extract plants, insuring a steady supply of Mead Chestnut Extract.

2. Why is Mead Chestnut Extract preferred over other tanning agents?

Mead Chestnut Extract is a superior tanning material, made by America's largest producer of vegetable tanning extracts. Repeated experience has shown:

A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

Ask about Mead Cold Soluble Chestnut Extract for retanned leathers. And—for more pounds of plumper leather—standardize on Mead Chestnut Extract.

IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield *(white weight basis)*
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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CHESTNUT
EXTRACT

THE MEAD CORPORATION
Tannin Extract Division, Lynchburg, Virginia

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SOLID	LIQUID	POWDERED
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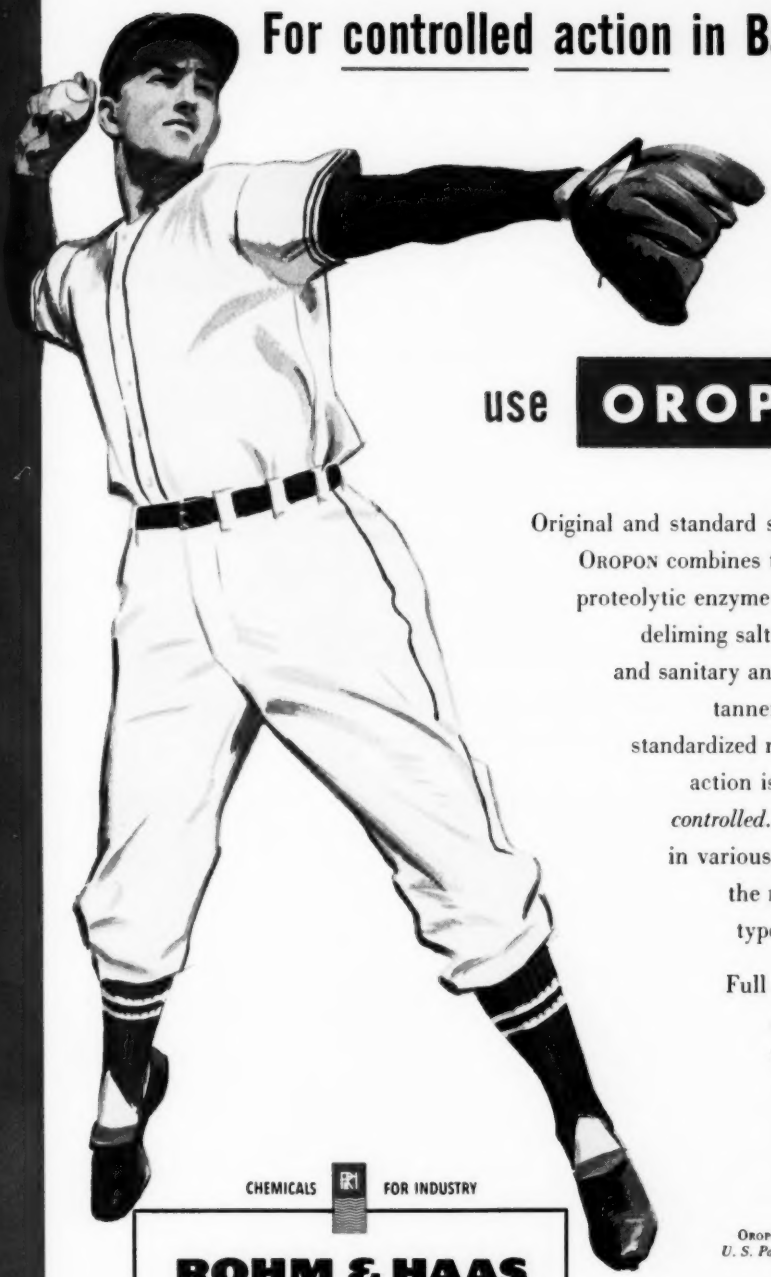

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Original and standard synthetic bate, OROPON combines the action of a proteolytic enzyme with that of a deliming salt. It is uniform and sanitary and provides the tanner with a clean, standardized material whose action is *automatically controlled.* It is available in various grades to suit the many different types of leathers.

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Sterozol is a non-coloring, non-interfering liquid which can be used in any wet operation:

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Sterozol's low relative toxicity, ease of handling, and economy have contributed in a large measure to its acceptance in the trade.

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Sebacol produces clean, uniform, quality leather under varied beamhouse practices.

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Biobate provides controlled, effective enzymatic action during bating for all types of leather.

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Save Hide Substance

USE.. BSM-11 or BUTROL

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BSM-11 is highly effective in controlling the growth of microorganisms which digest hide substance during processing. BSM-11 is a liquid, thus easily added to the systems directly from the drums.

It has been demonstrated in many tanneries that the synergistic combination of bactericides and fungicides in BSM-11 provides efficient, economical control of bacteria, molds and yeasts which damage skins and hides.

Our representative will give technical assistance on the most effective use of BSM-11 in your process.

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What Hooker Sodium Sulfhydrate does for the Leather you make...

SOLE LEATHER—With Hooker Sodium Sulfhydrate, you can increase sulfide strength of the unhairing solution just as desired, and still keep alkalinity low. This means easy unhairing in limited time. Hides are ready when desired—without loss of hide substance from long immersion. *Results:* a minimum of swelling . . . greater yield of tight, solid, smooth-grained leather . . . a significant saving of time and extra operations in the beam-house.

CALFSKINS AND HORSEHIDES—The tender grain of these skins is protected by Hooker Sodium Sulfhydrate from excessive swelling and plumping caused by high alkalinity. With Sodium Sulfhydrate, a minimum of swelling takes place, resulting in a better yield of fine, smooth leather.

GOATSKINS—Destructive bacterial action is held to a minimum, because Hooker Sodium Sulfhydrate increases the solubility of the lime and permits more constant pH value than with Sodium Sulfide. Sulfide content can be built up, with low alkalinity. Alkalinity can be increased or held as desired, without affecting sulfidity. *Result:* Greatly simplified control of quality, even with skins that vary widely in sensitivity.

When dissolved in lime, Hooker Sodium Sulfhydrate forms only half as much caustic soda as the same quantity of Sodium Sulfide forms. This gives you precision control of unhairing solutions—and many other advantages. Write today for a copy of Hooker Bulletin 500, "Sodium Sulfhydrate for the Leather Industry," which suggests unhairing procedures for various leathers.

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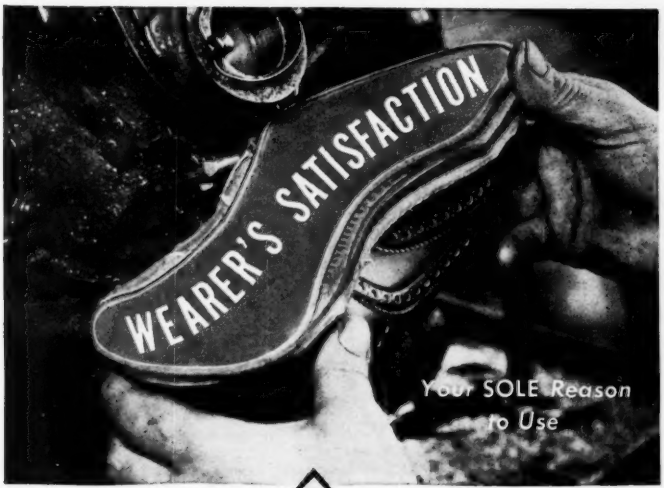

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Here's why. Diamond A does a *double* job — (1) It prepares sole leather for rolling and protects the grain. (2) Used as a dip after rolling, it toughens the grain and improves color and finish.

Why delay? Let the Borne, Scrymser representative give you full particulars on Diamond A. You'll agree it's in a class by itself.

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- *INDIVIDUAL THERMOSTATIC CONTROL FOR HEATERS*
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Thermoregulator: Fenwal expanding shell type.

Hot Plates: Cast aluminum alloy, 4 in. diameter.

Heating Units: Sheathed Chromalox, ring type; 300 watts; readily replaceable.

Base: 31 in. long, 9 in. deep, 8¾ in. high to top of heaters.

Rods: 36 in. long, ½ in. diameter, extending approx. 28 in. above heaters.

EXTRACTION APPARATUS, Electric, Thermostatic, Six-Unit, A.H.T. Co. Specification. Corrosion resistant throughout. Consisting of six separate heaters, each with individual thermostat for controlling temperatures at any point between 93°C and approx. 330°C, within ±5.5°C.

Each hot plate is equipped with individual switch and pilot lamp to facilitate setting. Mounted in a rectangular sheet metal base, with convenient clamping arrangement for six extraction apparatus of the Soxhlet type but useful for other laboratory procedures requiring variable temperatures.

5037-A. Extraction Apparatus, Thermostatic, as above described, complete with two crossarm supports, twelve cast aluminum clamps, two support rods, four clamp bar holders, and directions for use. Without connecting cord. Maximum power consumption 1800 watts.

For 115 volts a.c. **226.00**

5037-C. Ditto, but with one crossarm support, six clamps, and two clamp bar holders.

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JOURNAL OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

VOL. XLVIII MAY 1953 No. 5

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C. A. Ross, The Ohio Leather Co., Girard, Ohio.

SECRETARY'S NOTICE

Dr. Merrill has called to my attention that an error was made in the publication of the committees. We had listed Messrs. Wallace and Whitmore as members, but it should have been as follows—

Preparatory and Post-tanning Processes.....H. B. Merrill, Ch.

Subcommittees:

Committee on Beamhouse Methods.....William R. Roddy, Ch.
Committee on Testing of Fats, Oils, etc.....Merrill Leach, Ch.

FRED O'FLAHERTY, *Secretary.*

DOROTHY JORDAN-LLOYD MEMORIAL FELLOWSHIP

The Dorothy Jordan-Lloyd Memorial Committee of the British Leather Manufacturer's Research Association is offering a fellowship to a suitable American candidate.

The successful candidate will conduct research in the laboratories of the British Leather Manufacturers' Research Association near London, England. Transportation expenses and living expenses for one year will be provided.

Anyone considering himself a candidate, or anyone knowing a suitable candidate, please communicate with Dr. H. G. Turley, Rohm & Haas Company, 5000 Richmond Street, Philadelphia 37, Pa.

EMPLOYMENT BUREAU

Position Wanted: Experienced leather chemist and production man in calf or sheep skin. Has had experience in both chrome and bark.

O. MCLEAN, 412 Geneva Street, Ithaca, New York.

CORRECTION

The author has requested that the name of the tannery and laboratory of the Albert Trostel and Sons Company be added to the list of cooperating groups listed on page 69 of the February, 1953 issue of the Journal. This omission by the author occurred in the article by Lollar on the Analysis and Testing of Leather, *Jr. Amer. Lea. Chem. Assoc.* **48** 60 (1953).

COMMUNICATION TO THE EDITOR

LEATHER INDUSTRIES OF AMERICA
411 FIFTH AVENUE – NEW YORK 16, N. Y.
Walter Kraus, Director Murray Hill 6-7956

March 9, 1953

Mr. Dean Williams, Editor,
Journal of the American Leather Chemists Association
Ridgway, Pennsylvania
Dear Mr. Williams:

We are very much interested in obtaining data concerning any new scientific processes or work in progress designed to improve leather, and we would also like any other information dealing with technological developments in the tanning industry.

Much interest has been expressed in such information by editors, columnists, and writers, representing leading newspapers and magazines, and we feel that your members are in the best position to keep us posted on such developments.

One of the major functions of Leather Industries of America is to establish the modernity of leather and demonstrate how the tanning industry is continually benefitting from developments in chemistry and other fields of science. It would be most valuable for us to be in possession of any scientific data along these lines. Much of it will only be used as background or to answer specific inquires which frequently come to us from editors. Other developments, we hope, can be used to further document the technological strides which have been made in the tanning industry, and which can be expected to continue.

The assistance of the members of the American Leather Chemists Association in providing us with suitable material will be very much appreciated.

Very truly yours,

(s) WALTER KRAUS

The foregoing letter was considered of sufficient interest to the A.L.C.A. membership to warrant its publication in the Journal. Mr. Kraus, Director of Leather Industries of America, is soliciting suggestions or information from our membership which may help the L.I.A. in its work of promoting the demand and use of all types of leather. All communications on the subject should be addressed to Walter Kraus, Director, Leather Industries of America, 411 Fifth Ave., New York 16, N. Y.

A.L.C.A. DELEGATES TO THE INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

Dr. Turley, President of the Association, has appointed the following as delegates to the Barcelona Conference.

Ira D. Clark E. S. Flinn A. N. Kay M. Maeser
F. O'Flaherty C. G. Telander H. G. Turley

COUNCIL MEETING MINUTES

A meeting of Council was held at the Hotel Sylvania, Philadelphia, Pa., February 12, 1953.

The meeting was called to order at 10:00 A. M. by President Turley. Present were Messrs. Flinn, O'Flaherty, Windus, Hobbs, Morrison and Ross.

The minutes of the meeting on November 13th were given final approvement.

A list of nominees, as presented by the Nomination Committee and as published in the February issue of the Journal, was approved. Council requested the Secretary to advise the Nominating Committee, consisting of Messrs A. Fleisch, David Wilson and Robert Adams, that their committee was now discharged and to express to them appreciation for the work which they did.

The President will appoint a new Nominating Committee for the year of 1953.

Dr. Turley reported that, under the advice of Dr. H. B. Merrill, Chairman of our Selection Committee, he had offered the Dorothy Jordan-Lloyd fellowship to Mr. Myron Robinson of the Bureau of Standards. We are awaiting Mr. Robinson's decision. Dr. Hobbs will discuss the matter with Mr. Robinson.

Mr. Dean Williams reported for the year 1953 and also upon the status of the material which he still has for publication. Mr. Williams also reported that he had not yet received from Mr. D. Lord the stenographic copy of the proceedings of the 1952 symposium of the New England Tanners' Club.

Council instructed Mr. Dean Williams that if people request reprints with covers that he should determine the extra cost and they then should pay the extra charge on the same basis as additional reprints. Mr. Williams was instructed to prepare a new order sheet, giving the author a choice of reprints with or without covers.

Dr. Flinn reported for the Technical Committees, and the substance of his report will be published as a separate matter in the Journal.

The Secretary read a list of thirteen resignations by members and a list of thirty members who were dropped for non-payment of dues in 1952.

The budget as follows was presented by Mr. Teas, Chairman of the Ways and Means Committee, and was approved by Council.

	1952 Proposed Budget	1952 Actual Budget	1953 Proposed Budget
GENERAL ACCOUNT: INCOME			
Dues	$10,000.00	$10,532.50	$10,500.00
Interest on United States Bonds	725.00	915.68	915.00
By-Laws and Methods	–0–	–0–	–0–
Annual Meeting	–0–	–0–	–0–
Directory	600.00	701.20	700.00
Total	$11,325.00	$12,149.38	$12,115.00
GENERAL ACCOUNT: EXPENSE			
Executive Secretary's Salary	$ 4,000.00	$ 3,999.92	$ 4,000.00
Secretary's Office Expense	1,000.00	998.44	1,000.00
Annual Meeting	100.00	161.91	150.00
Committee Work	100.00	11.30	100.00
Council Meeting	200.00	131.79	200.00
Auditing	100.00	100.00	100.00
Printing Methods & By-Laws	1,000.00	–0–	1,000.00
Printing Directory	600.00	800.50	800.00
Reserve for Uncollectible Accounts	300.00	387.90	400.00
Winheim Award	–0–	–0–	100.00
Total	$ 7,400.00	$ 6,591.76	$ 7,850.00
Surplus on General Accounts	$ 3,925.00	$ 5,557.62	$ 4,265.00
JOURNAL ACCOUNT: INCOME			
Advertisements	$11,000.00	$11,899.61	$11,000.00
Subscriptions	4,500.00	4,810.10	5,200.00
Journals, Volumes, Reprints, Sold	3,000.00	1,822.78	1,500.00
Dues, S.L.T.C., Difference	500.00	816.00	800.00
Total	$19,000.00	$19,348.49	$18,500.00
JOURNAL ACCOUNT: EXPENSE			
Printing and Publishing	$16,000.00	$16,258.34	$16,000.00
Printing Reprints	2,000.00	1,417.20	2,000.00
Copyright, Insurance, Storage	500.00	460.00	500.00
Abstracts and Translations	300.00	314.01	300.00
Editor's Salary	900.00	900.00	900.00
Editor's Office Expense	600.00	549.83	900.00
Total	$20,300.00	$19,899.38	$20,600.00
Deficit on Journal Account	$ 1,300.00	$ 550.89	$ 2,100.00

It was suggested by Mr. Morrison that some effort be made to get some of the advertisers to change the composition of their ads from time to time so as to make the Journal more attractive.

Upon the recommendation of the Chairman of the Ways and Means Committee it was approved that the Secretary purchase $5,000.00 U. S. Bonds with cash on hand at the moment.

The following candidates were elected to active membership:

Mr. Malcom H. Battles	Mr. Mark Luckens
Mr. Thomas G. Harris	Dr. Thomas L. Reissmann

The following member transferred his membership to active—

Mr. Charles Knisely

Dr. Blackadder was presented by Dr. Turley with a Certificate of Honorary Membership, in recognition of Dr. Blackadder's past services to the industry and to the Association. Dr. Blackadder expressed his very grateful thanks for this symbol of recognition.

Dr. Wallace Windus was appointed Chairman of the Awards Committee. He will select two more members who will be approved by Council.

Dr. Turley will appoint the delegates to the International Union of Leather Chemists Societies.

Mr. Walter Kraus, Director of the Leather Industries of America, spoke about the plans which they had on the occasion of the Fiftieth Anniversary Meeting of the Association.

Mr. Robert Hague will notify Mr. W. Kraus so that publicity in connection with the American Leather Chemists Association Golden Jubilee Meeting will be handled by Mr. Kraus.

Dr. Kirk then reviewed the plans which were in progress for making the Fiftieth Anniversary Meeting an outstanding one. Mr. Meo spoke on the program that they were making on the social aspects on the meeting and Mr. Hague reported for the Publicity Committee. Dr. Kirk advised that he had appointed Mrs. Boss to be in charge of the social activities for the women and that she is working on this.

Dr. Kirk presented the following proposed budget which was approved by Council:

1. Printed Matter—				
Publicity			$500.00	
Programs			150.00	
Badges			100.00	
Speaker Certificates			50.00	
Total expense of printed matter				$ 800.00
2. Invited Guests—				
	Transportation	Hotel		
Dr. Phillips	$600.00	$80.00		
Dr. Gustavson	100.00	80.00		
Prof. Chambard	100.00	80.00		
Dr. Pauling	300.00	80.00		
Total expenses of invited guests				$1,420.00
3. Golf Committee			$500.00	500.00

4.	Ladies Committee	300.00	300.00
5.	Social Committee—		
	Formal	$300.00	
	Party	800.00	
	Total expense of social committees		$1,100.00
6.	Hotel—		
	Gratuities	$150.00	
	Flowers	75.00	
	Total expense at hotel		225.00
7.	Banquet Expense	$ 50.00	50.00
8.	Transcript Operator	250.00	250.00
			$4,645.00

Council also approved the registration fee of $8.00 for members and $16.00 for non-members.

Consideration was then given to the meeting place for 1954. Dr. Kirk was delegated to look into several resorts to determine whether or not open dates were available in 1954.

Luncheon was held at 12:30 P. M. and because there was a simultaneous meeting of the Tannin Analysis Committee the members of this committee joined with Council at luncheon.

A letter of invitation was read to Council and visiting committee members from Mr. Jerome Rogers, Secretary-Treasurer of the Delaware Valley Tanners' Club, inviting all persons present to attend the meeting of the Delaware Valley Tanners' Club on Thursday, February 12th.

There being no further business the meeting adjourned at 3:30 P. M.

Respectfully submitted,

FRED O'FLAHERTY, *Secretary.*

AUDITOR'S STATEMENT

February 19, 1953

The American Leather Chemists Association, Inc.
The University of Cincinnati
Cincinnati, Ohio

Gentlemen:

In accordance with the request of Dr. Fred O'Flaherty, Secretary-Treasurer, we have examined the balance sheet of the American Leather Chemists Association, Incorporated, as of December 31, 1952, and the related statements

of income and surplus for the year then ended. Our examination was made in accordance with generally accepted auditing standards, and accordingly included such tests of the accounting records and such other auditing procedures as we considered necessary in the circumstances.

The report of the examination is presented herewith, together with the following exhibits and schedules:

Exhibit I: Balance sheet at December 31, 1952, and comparison with December 31, 1951.

Exhibit II: Statement of income for the year ended December 31, 1952, and comparison with the year ended December 31, 1951.

Exhibit III: Statement of surplus for the year ended December 31, 1952, and comparison with the year ended December 31, 1951.

The commercial account balance on deposit with the Central Trust Company was confirmed independently and was reconciled with the cash account balance of the Association.

Accounts receivable were not circularized; this procedure was considered unnecessary in view of the small balance of each account, and in view of the fact that of the accounts receivable amounting to $2,851.20 at December 31, 1952, approximately ninety per cent of the total was collected in January 1953. By other auditing procedures, we have satisfied ourselves of the accuracy and the validity of the receivables.

The United States War Bonds, Series F; the United States Treasury Bonds of the series 1967–1972; and the United States Treasury Bonds, Series G, were confirmed by Dr. Fred O'Flaherty. All bonds are in the safe deposit box at the Central Trust Company. In 1952 United States Treasury Bonds were purchased at a cost of $4,839.06.

Accumulated interest on the Series F War Bonds has been added to the original cost of the bonds. The total accumulated value of the Series F War bonds at December 31, 1952 is $11,444.00, of which $1,824.00 represents accumulated interest. In the year 1952, all bond investments earned interest of $915.68.

Dues received in advance totaling $224.00, and subscriptions received in advance totaling $2,540.01, were verified in detail and were reconciled to the controlling accounts.

Net profit for the year ended December 31, 1952 was $4,718.36, compared with $5,043.10 for the year ended December 31, 1951, or a decrease of $324.74. The causes of the decreased profit are analyzed in Exhibit II. In the year 1952, revenues increased $2,914.94, and expenses increased $3,239.86. The net profit is satisfactory for all purposes.

In our opinion the accompanying balance sheet and related statements of income and surplus present fairly the financial position of the American Leather Chemists Association, Incorporated, at December 31, 1952, and the results of its operations for the year then ended, in conformity with generally accepted principles of accounting, applied on a basis consistent with that of the preceding year.

Respectfully submitted,

ARTHUR W. HOLMES,
Certified Public Accountant.

EXHIBIT I

THE AMERICAN LEATHER CHEMISTS ASSOCIATION, INC.

BALANCE SHEET AT DECEMBER 31, 1952
AND COMPARISON WITH DECEMBER 31, 1951

ASSETS

	December 31, 1952	December 31, 1951	Increase or *Decrease* 52 over 51
CURRENT ASSETS:			
Cash on hand and in bank	$14,282.14	$14,476.92	$ *194.78*
Accrued interest on Treasury Bonds	62.50	62.50	–0–
Accrued receivable, advertisers	2,837.45	2,074.61	762.84
Accounts receivable, reprints	13.75	263.70	*249.95*
Total current assets	$17,195.84	$16,877.73	$ 318.11
INVESTMENT SECURITIES:			
United States war bonds, series F, at cost of $9,620.00, plus $1,824.00 of accrued interest	$11,444.00	$11,076.00	$ 368.00
United States Treasury bonds, 2.5% series of 1967–1972, at cost	13,000.00	13,000.00	–0–
United States Treasury bonds, 2.5% series G, July 1948 at cost	5,000.00	5,000.00	–0–
United States Treasury bonds, 2.5% series of 1967–1972, at cost	4,839.06	–0–	4,839.06
Total investment securities	$34,283.06	$29,076.00	$ 5,207.06
Total Assets	$51,478.90	$45,953.73	$ 5,525.17

LIABILITIES AND CAPITAL

CURRENT LIABILITIES AND DEFERRED CREDITS:			
Accounts payable	$ 1,587.30	$ 1,158.44	$ 428.86
Income tax withheld	140.40	94.20	46.20
Dues received in advance	224.00	376.35	*152.35*
Subscriptons received in advance	2,540.01	2,055.91	484.10
Total Liabilities	$ 4,491.71	$ 3,684.90	$ 806.81
CAPITAL:			
Earned surplus (Exhibit III)	$46,987.19	$42,268.83	$ 4,718.36
Total liabilities and capital	$51,478.90	$45,953.73	$ 5,525.17

EXHIBIT II

THE AMERICAN LEATHER CHEMISTS ASSOCIATION, INC.

STATEMENT OF INCOME

FOR THE YEARS ENDED DECEMBER 31, 1952 AND DECEMBER 31, 1951

	December 31, 1952	December 31, 1952	Increase or *Decrease* 52 over 51
GENERAL REVENUES:			
Dues, Journal subscriptions included	$10,532.50	$ 8,827.53	$ 1,704.97
By-laws and methods booklet	–0–	117.90	*117.90*
Directory	701.20	495.49	205.71
Interest income	915.68	725.00	190.68
Total general revenue	$12,149.38	$10,165.92	$ 1,983.46
JOURNAL REVENUES:			
Advertising	$11,899.61	$10,319.32	$ 1,580.29
Subscriptions	4,810.10	4,112.06	698.04
Journal sales	533.59	1,310.38	*776.79*
Reprints	1,289.19	2,032.00	*742.81*
Dues, S.L.T.C.	816.00	643.25	172.75
Total Journal revenue	$19,348.49	$18,417.01	$ 931.48
Total Revenue	$31,497.87	$28,582.93	$ 2,914.94
GENERAL EXPENSES:			
Secretary expense	$ 3,999.92	$ 3,569.59	$ 430.33
Office operating expense	998.44	794.92	203.52
Uncollectible accounts expense	387.90	255.00	132.90
Directory expense	800.50	521.50	279.00
Annual meeting expense	161.91	–0–	161.91
Council meeting expense	131.79	176.17	*44.38*
Weinheim award	–0–	100.00	*100.00*
Auditing	100.00	100.00	–0–
Association emblems	–0–	(13.50)	13.50
Leather Chemists Union dues	117.60	117.60	–0–
President's expense	–0–	69.22	*69.22*
By-laws and methods	–0–	130.00	*130.00*
Total general expense	$ 6,698.06	$ 5,820.50	$ 877.56
JOURNAL EXPENSES:			
Printing	$16,258.34	$13,741.94	$ 2,516.40
Editor's compensation	900.00	900.00	–0–
Editor's expense	549.83	502.92	46.91
Insurance	62.00	58.00	4.00
Storage	350.00	350.00	–0–
Miscellaneous	83.50	137.41	*53.91*
Copyright registrations	48.00	48.00	–0–
Reprints	1,417.20	1,751.85	*334.65*
Exchange charges	2.86	3.76	*.90*
Translations and abstracts	314.01	208.77	105.24
Committee expense	11.30	16.68	*5.38*
Discounts allowed	84.41	–0–	84.41
Total Journal expense	$20,081.45	$17,71933.	$ 2,362.12
Total Expense	$26,779.51	$23,539.83	$ 3,239.68
Net Profit	$ 4,718.36	$ 5,043.10	$ *324.74*

DISTRIBUTION OF NET PROFIT:			
General, profit	$ 5,451.32	$ 4,345.42	$ 1,105.90
Journal, profit or (loss)	-(732.96)	697.68	*1,430.64*
Total net profit	$ 4,718.36	$ 5,043.10	$ *324.74*

EXHIBIT III

THE AMERICAN LEATHER CHEMISTS ASSOCIATION, INC.

STATEMENT OF SURPLUS

FOR THE YEARS ENDED DECEMBER 31, 1952, AND DECEMBER 31, 1951

	December 31, 1952	December 31, 1951	Increase or *Decrease*
Balance, January 1	$42,268.83	$37,225.73	$ 5,043.10
Add net profit or deduct net loss:			
General	5,451.32	4,345.42	1,105.90
Journal	*-732.96*	697.68	*1,430.64*
Balance, December 31	$46,987.19	$42,268.83	$ 4,718.36

Studies on the Polar Amino Acid Content of Collagen and Related Material

By J. CASSEL, E. MCKENNA, and A. GLIME

National Bureau of Standards

ABSTRACT

Analyses have been made of the polar amino acid content of collagen, hide powder, and gelatin. The acidic amino acids of hide powder were determined by two chromatographic procedures. The glutamic acid content of the three materials was also estimated by conversion of this amino acid to pyrrolidone carboxylic acid.

The acidic and basic amino acid analyses were made on hide powders which had been modified by deamination, methylation, formaldehyde tanning and by treatment with trypsin, and on a chrome tanned leather.

No significant differences were found in the amino acid analyses of collagen, gelatin, or hide powder. The amino acid content of hide powder was not altered by chrome or vegetable tanning or by treatment with trypsin. Deamination treatment for one week reduced the lysine content by eighty per cent while prolonged treatment reduced the arginine value. The aspartic acid value of methylated hide powder was considerably lower than that of the untreated material.

I. INTRODUCTION

Because of their chemical reactivity, the polar amino acids are the most important of the amino acids found in protein. These include the acidic amino acids, glutamic and aspartic, and the basic amino acids, lysine, arginine, and histidine. It is generally accepted that these amino acids exist in the

protein with their reactive side chains free and projecting from the polypeptide backbone as active centers. Consequently they have been assigned primary roles in physical and chemical phenomena such as adsorption, solubility phenomena, and chemical reactivity. Because of their importance in reactions, rapid and yet accurate methods of analysis of these amino acids are desirable.

Collagen which is relatively rich in polar amino acids is the most abundant protein of skin. It constitutes the bulk of the substance of the white fibers of the connective tissues of the derma and is of extreme importance in the process of tanning. It is generally accepted that the polar amino acid side chains play a primary role in this process of leather making.

Until a few years ago the analysis for these acids was accomplished by gravimetric means which were exacting and time consuming and which with the acidic amino acids gave apparently lower results than would be predicted from the titration curves of the materials analyzed. In 1948 Stubbings and Theis [1] reported a chromatographic method of separating the acidic and basic amino acids of a collagen hydrolysate. The individual amino acids were quantitatively estimated by various color reactions. This technique was reported to give results in a minimum of time and required neither elaborate equipment nor highly trained personnel.

This paper presents data obtained by this method (referred to as method 1) on the acidic and basic amino acid content of collegen, gelatin, hide powder, and of several modified hide powder samples. While the method used by Stubbings and Theis gives satisfactory results with the basic amino acids, it has certain limitations when used for the analysis of the acidic amino acids. For this reason experimentation with another chromatographic procedure (method 2) is reported and in addition the glutamic acid analysis of collagen, gelatin, and hide powder as obtained by the method of Olcott [2] is given. This latter method consists essentially of an amino nitrogen analysis of a protein hydrolysate before and after the glutamic acid has been converted to pyrrolidone carboxylic acid.

2. Materials

The collagen analyzed during these experiments was a highly purified grade prepared from steer corium by the method of Highberger [3]. The hide powder and gelatin were commercial products.

Deaminized hide powder was obtained by suspending hide powder in a mixture of glacial acetic acid and sodium nitrite at 15 °C. through which carbon dioxide was constantly bubbled to provide proper agitation and to keep the formation of nitric acid to a minimum [4].

Methylation of hide powder was accomplished by a method similar to that of Blackburn et al [5]. Twenty-five grams of hide powder were shaken with 250 ml of a molar sodium acetate buffer (pH 7.5) and 12 ml of dimethyl sulfate

for one hour. The liquid was then drained from the hide powder, fresh solutions added and the mixture stirred again for an hour. This procedure was repeated a dozen times. To reduce the extreme swelling of the methylated powder, it was placed in a 10 per cent solution of sodium chloride for a day, then rinsed with distilled water until free of Cl^-, and dehydrated with acetone and alcohol.

Hide powder was also treated with a 0.1 per cent trypsin solution, buffered with calcium carbonate (pH 8.0), for five hours at 35°C. The product was thoroughly washed with distilled water and dehydrated with acetone and alcohol.

Formaldehyde tanned hide powder was prepared by the method of Highberger and Retzsch [6] with the exception that the material was washed thoroughly in changes of 0.1 M phosphate buffer before washing in several changes of distilled water. The chrome tanned sample was a degreased, water leached, hydraulic packing leather from which the grain layer had been removed by splitting.

For analysis each material was hydrolyzed to amino acids by autoclaving at 130°C for six hours in 6*N* hydrochloric acid. The cooled hydrolysate was filtered to remove any humin formed during hydrolysis and then vacuum distilled three times to remove excess hydrochloric acid.

The aluminum oxides which proved most satisfactory for the chromatographic procedures were a grade purified according to Brockman [7] and a Merck product prepared for chromatographic adsorption (aluminum oxide Reagent 71707). The column used in the separation of the basic amino acids was a mixture of Hyflo Super Cel and Fuller's Earth.

3. Methods and Analysis

3.1 *Chromatographic Method* 1

Method 1 is similar to the method used by Stubbings and Theis. Standard amino acid solutions were prepared with amino acid concentrations, respectively greater and less than the expected amino acid content of the protein hydrolysate. The total amino acid concentration of the hydrolyzate was approximately 10 milligrams per milliliter. Ten ml. of the amino acid solutions and of the hydrolyzate, both neutralized to pH 7 were percolated through twenty grams of acidified (acetic acid) aluminum oxide in columns. After allowing fifteen minutes for adsorption of the amino acids, the neutral and basic fractions were removed by elution with water, the glutamic acid was eluted with 0.5*N* acetic acid and the aspartic acid with 0.5*N* alkali. When using the aluminum oxide products mentioned earlier, it was found necessary to use 150 ml. of water for the elution of the neutral and basic fraction and 150 ml. of acetic acid for the elution of glutamic acid. The neutral and basic fraction was reduced in volume, acidified, and adsorbed on the Fuller's Earth-Super Cel column. In agreement with the work of Doty [8] it was found

unnecessary to remove the acidic fraction by the aluminum oxide treatment before adsorption in the basic column had occurred. From the basic column the neutral (and acidic if present) amino acids were eluted with 0.5*N* hydrochloric acid, lysine with normal hydrochloric, and arginine and histidine with a ten per cent solution of pyridine in hydrochloric acid.

The amino acids were then estimated colorimetrically, using as standards the eluted fractions obtained from known solutions. Lysine, glutamic, and aspartic acids were determined by the nonspecific ninhydrin test [8, 9], arginine by a modification of the Sakaguchi reaction [10], and histidine by the diazotization reaction of McPherson [11].

3.2 *Chromatographic Method* 2

A method similar to that of Turba and Richter [12] was used to separate the acidic amino acids. Six grams of aluminum oxide were pretreated with a 1*N* acetate buffer of pH 3.3 and then transferred with water into a chromatographic tube (7 x 1.5 cm.). The hydrolyzate derived from the acid hydrolysis of four grams of protein was distilled in vacuo to remove excess hydrochloric acid. Before making the hydrolyzate to volume (100 ml.) its pH was adjusted to 3.3. A two milliliter aliquot was added to the aluminum oxide column and a head of liquid was maintained at all times on the column. After adsorption of the amino acids had occurred, the neutral and basic fractions were eluted with 100 milliliters of water. The column was dried by suction and transferred to a Buchner fritted disk. The aluminum oxide was then treated seven times with twenty milliliter portions of 0.05*N* sodium hydroxide. After each addition of alkali the aluminum oxide was thoroughly stirred with a glass rod, allowed to settle for two minutes and finally the solution was removed by suction. The glutamic and aspartic acids were thus extracted together.

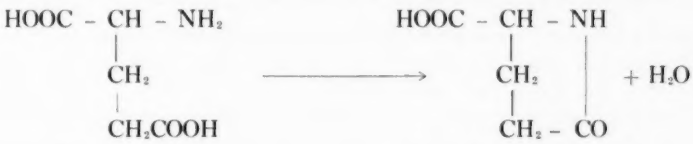
The alkaline solution containing glutamic acid and aspartic acid was reduced to twenty-five milliliters by vacuum distillation and the pH was adjusted to 3.3. Aliquots were then used for the determinations of amino nitrogen [13] and the "carboxyl" nitrogen [14].

The procedure differs from that of Turba and Richter who used a second adsorption of acids and separation of the glutamic acid from the aspartic acid by elution of the former with dilute acetic acid and the latter with dilute alkali.

3.3 *Determination of Glutamic Acid*

Glutamic acid was also determined by conversion to pyrrolidone carboxylic acid. The method of Olcott [2] was followed except that after hydrolyzing one gram of protein the excess hydrochloric acid of the protein hydrolyzate was removed by vacuum distillation. The pH of the hydrolyzate was then adjusted to 3.3 and made to 100 milliliters. One aliquot was used for the

amino nitrogen determination. A second aliquot was used for the conversion of the glutamic acid to pyrrolidone carboxylic acid. This conversion was accomplished by autoclaving for four hours at 20 lb. pressure and 126°C. Olcott found that 92 per cent of the glutamic acid (I) is converted under these conditions to pyrrolidone carboxylic acid (II). The reaction is given below:



Glutamic Acid (I) — Pyrrolidone Carboxylic Acid (II)

The extent of conversion was calculated from the change in the amino nitrogen content of the autoclaved sample from that of the sample before autoclaving; the nitrogen being directly proportional to the glutamic acid content. Control experiments with known quantities of glutamic acid and the amino acids normally present in the hydrolyzates of collagen showed that 93 per cent of the glutamic acid undergoes this reaction.

4. Results and Discussion

4.1 *Basic Amino Acid Analysis of Collagen, Hide Powder, and Gelatin*

The basic amino acid analyses by chromatographic method 1 of four collagen, four hide powder, and two gelatin hydrolyzates, are shown in Table 1. A measure of the precision is indicated by the standard deviations recorded for each amino acid. It is to be noted that the highest precision is observed in the determination of histidine which is present in rather small quantities in these materials. Poorest precision is found for lysine. After chromatographically separating lysine from arginine and histidine, it was estimated quantitatively by the nonspecific ninhydrin reaction. This technique makes no attempt to separate hydroxylysine from lysine. The individual and total basic values are in good agreement with those listed by Block and Bolling [15] as "best values" for gelatin.

TABLE I

Basic Amino Acid Analysis of Collagen, Hide Powder and Gelatin

	Collagen-a	Hide Powder-a	Gelatin-b	Standard deviation of individual hydrolyzate
Lysine, %	5.4	5.2	5.7	0.40
Arginine, %	9.0	8.6	8.7	0.28
Histidine, %	0.77	0.76	0.74	0.03

a. Average of four hydrolyzates.
b. Average of two hydrolyzates.

The data show that these three materials, collagen, hide powder and gelatin, which differ considerably in appearance, do not differ significantly in their basic amino acid analysis. A discussion of this observation is included with the discussion of the acidic amino acid analyses of these same materials.

4.2 *Acidic Amino Acid Analysis of Collagen, Hide Powder, and Gelatin*

In Tables 2 and 3 are given the results of the acidic amino acid analysis of collagen, hide powder, and gelatin by the several techniques described earlier in this paper. Included with these data are values for these materials recorded in fairly recent literature. With the exception of the results obtained using chromatographic method 2, the data obtained for these three protein materials agree well with values recorded in the literature. It is to be noted that the gravimetric values recorded in the literature are approximately half the values obtained by the more recent techniques of chromatography and microbiology. This arises from high losses inherent in the precipitation used in the gravimetric analysis.

TABLE II

Glutamic Acid Analysis of Collagen, Hide Powder, and Gelatin
(Results expressed in per cent)

	Method			
	Chromatographic method 1	Olcott	Chromatographic method 2	Literature values
Collagen	12.0a	12.2d		11.6[1] 12.4[4]e 11.4[25]f 5.7[26]g
Hide Powder	11.9a	12.3c	14.2b	11.7[1]
Gelatin	12.1d	12.4d		11.4[25]f 5.8[27]g
Standard deviation of individual hydrolyzate	0.42	0.25	0.26	

a. Average of 7 hydrolyzates.
b. Average of 4 hydrolyzates.
c. Average of 5 hydrolyzates.
d. Average of 2 hydrolyzates.
e. These values obtained chromatographically have been corrected by the recovery factor suggested by the authors.
f. Microbiological value.
g. Gravimetric method.

The data show collagen, hide powder, and gelatin do not differ appreciably in their dicarboxylic acid content. Results given in Table I show that there is no significant difference in the basic amino acid analysis of these same materials. Although a similarity in the amino acid content of these materials

TABLE III

Aspartic Acid Analysis of Collagen, Hide Powder, and Gelatin

(Results expressed in per cent)

	Chromatographic method 1	Chromatographic method 2	Literature values
Collagen	6.0a		6.0[1]
			6.5[4]d
			7.0[25]e
			3.8[28]f
			3.5[26]f
Hide powder	6.3a	4.7b	6.1[1]
Gelatin	6.7c		3.4[27]
Standard deviation of an individual hydrolyzate	0.37	0.15	

a. Average of 7 hydrolyzates.
b. Average of 4 hydrolyzates.
c. Average of 2 hydrolyzates.
d. These values obtained chromatographically have been corrected by the recovery factor suggested by the authors.
e. Microbiological value.
f. Gravimetric method.

has been assumed before, it is still rather surprising when one considers the processes by which the hide powder and gelatin are prepared. Preparation of hide powder involves prolonged and rather severe treatment with lime solutions for the removal of hair. Stubbings and Theis[1] showed that no significant change occurs in the polar amino acid content of a green salted hide during the depilation process, either in the lime slurry or in a highly alkaline caustic bath. The preparation of commercial gelatin from collagen generally involves either acid or alkali treatment of the collagen. Ames[16] has stated that only those gelatins are stable which have been prepared from acid or alkali treated collagens. The similarity of the diamino and dicarboxylic acid content of collagen, hide powder, and gelatin, indicates the stability of the peptide bonds which bind these amino acid residues into the polypeptide chains. Except for the hydrolysis of acid amide groups to carboxyl units, the residue side chaines are very resistant to degradation. The only apparent difference in the collagen, hide powder, and gelatin, is in their amide values of 0.6, 0.4, and 0.2 per cent, respectively.

The precision of the techniques used for the dicarboxylic acid analyses is indicated by the standard deviations expressed for an individual hydrolyzate. The precision of chromatographic method 1 is not as good as that of the Olcott method or chromatographic method 2. Chromatographic method 1 relies on the ability of an aluminum oxide column to separate the glutamic acid from the aspartic acid. Any tailing of the glutamic into the aspartic zone would affect the results. By simultaneously carrying out the analysis of

the standard amino acid solutions with the protein hydrolyzate, this difficulty is minimized but not eliminated completely due to the variability in the aluminum oxide columns.

To reduce the tailing of the glutamic into the aspartic zone the length of the aluminum oxide column was increased 40 per cent (28 grams vs 20 grams) and the column pretreated with an acetate buffer in preference to dilute acetic acid. The intermingling tendency of these acids depended to some extent on the percolation rate of the eluents. Drake[17] has pointed out that front and rear boundaries are usually not sharp in elution procedures. He observed that best results were obtained with flow rate between high speed with lack of equilibrium and low speed with appreciable diffusion. It has been found imperative to maintain constant flow rates in the standard and hydrolyzate columns and that better precision was attained using the slowest flow rate obtainable with a suction pump.

In chromatographic method 1, one very obvious difficulty is encountered when eluting the aspartic acid with dilute alkali. Aluminum ion is carried along, and is precipitated as colloidal aluminum hydroxide when the extract is neutralized. This must be removed by centrifuging before colorimetric analyses can be made. This rather bulky precipitate occludes some aspartic acid and the precision of the method is undoubtedly affected by this step. This interference was reduced to a minimum by adding citric acid to form a soluble aluminum complex in the eluate. It was then necessary to dilute with water rather than alcohol in the colorimetric procedure, in order to avoid colloidal precipitation during the ninhydrin color test.

The better precision observed with the Olcott method and chromatographic method 2, would seem to be due to the fact that in neither of these methods is there any attempt made to separate the aspartic acid from the glutamic. The Olcott method simply requires an amino nitrogen determination on a protein hydrolyzate before and after a four hour autoclave treatment at a pH suitable for conversion of the glutamic acid to pyrrolidone carboxylic acid. Since the estimate of glutamic acid in this instance depends on the accuracy in determining a small difference in two relatively large amino nitrogen values, a very accurate amino nitrogen apparatus is required. The Van Slyke manometric equipment was found to be very satisfactory in this respect. The Olcott method is particularly applicable to collagen, hide powder, and gelatin which have no cystine and require no correction for its interference. The data of Table 2 show that this method and that of Stubbings gave glutamic acid values which did not differ significantly.

While the precision of chromatographic method 2 is excellent for both aspartic and glutamic acid, the values for the former are considerably higher and the values for the latter considerably lower, than results obtained by the two methods previously discussed or those reported in literature. In this procedure no synthetic standard amino acid solutions were analyzed simul-

taneously with the unknown hydrolyzate. The glutamic and aspartic acids were eluted as one fraction and the analysis of this fraction was based on the difference in behavior of these two acids toward ninhydrin at a pH of 2.5 and a temperature of 100°C. Van Slyke and collaborators [14] found that aspartic acid under these conditions liberated two moles of carbon dioxide per mole of acid, while one mole of glutamic liberates only one mole of carbon dioxide. The deamination procedure of Van Slyke [13], on the other hand, with both acids liberates one mole of amino nitrogen per mole of acid. Therefore, estimation of the acids is permitted in the presence of each other.

The discrepancy in the results obtained by this method as compared with those referred to previously would seem primarily to be due to the simultaneous elution of an amino nitrogen containing contaminant, the presence of which would inflate the α amino nitrogen value and consequently yield a high glutamic acid and low aspartic acid value. The solutions were vacuum distilled after being made basic with magnesium oxide in order to liberate any ammonia which might be present as a contaminant. This did not influence the results, so presumably no ammonium chloride has been eluted with these acids.

Attempts to use the micro method of West, Christensen, and Rinehart [18], for the estimation of carbon dioxide liberated in the ninhydrin reaction were not satisfactory. A second titration method recommended by Van Slyke, etc. [19] for estimating this carbon dioxide was unsatisfactory also, since small variable amounts of acetic acid derived from the chromatographic column were volatilized in the ninhydrin reaction and vitiated the titration. In the Van Slyke manometric procedure finally adopted for carbon dioxide and amino nitrogen determinations, the pressure exerted by the carbon dioxide alone was very accurately measured, since any interfering volatile materials were excluded from the apparatus during the determination.

Although the glutamic and aspartic values of hide powder as determined by chromatographic method 2 do not agree with those discussed previously, it should be noted that the total dicarboxylic acid content is not significantly greater than that determined by the other methods, and is very much in line with that calculated from titration curves of Bowes and Kenton [20], i. e., 1.32 millimoles of dicarboxylic acid per gram of protein.

4.3 *Acidic and Basic Amino Acid Analysis of Modified Hide Powder and Related Material*

The results of the analyses of the acidic and basic amino acids are listed in Table 4 for several samples of modified hide powder and several tanned hide powder samples. These analyses were made by chromatographic method 1. While the glutamic acid values do not differ significantly from that of hide powder, the aspartic acid results from the methylated and chrome tanned samples are lower than that of hide powder (see tables 2 and 3). The chrome

aspartic acid value is approximately two standard deviations below the hide powder value. The methylated sample is on the other hand significantly lower in its aspartic acid content.

TABLE IV

Acidic and Basic Amino Acid Analysis of Modified Hide Powders*

(Results expressed in per cent)

	Deaminized		Treated with trypsin	Methylated	Formaldehyde tanned	Chrome tanned
	1 day	1 week				
Glutamic	12.0	11.5	11.4	11.4	12.3	12.2
Aspartic	6.6	6.0	6.6	4.9	6.5	5.4
Lysine	0.95	0.55	5.4	5.1	5.1	5.1
Arginine	8.4	6.6	8.7	8.2	8.1	9.2
Histidine	0.74	0.70	0.78	0.36	——	0.80

*The chrome sample was not prepared from hide powder but is a commercially tanned piece of hide from which the grain layer was split off and the remaining portion degreased and then leached in water.

Current work at the National Bureau of Standards[21] has shown that aspartic acid exists in collagen primarily as a monoamide. Partridge and Davies[22] showed that heating gelatin with a weak acid such as oxalic or acetic would preferentially release aspartic acid into solution before any other ninhydrin reacting substances are liberated. The existence of the aspartic acid in collagen as an amide and its preferential release to solution by weak acids might imply that this amino acid residue is exposed and vulnerable to hydrolysis. Any sulfuric acid which was liberated from the methylating agent, dimethyl sulfate, and the effect of which was not immediately nullified by the acetate buffer, might conceivably attack the exposed aspartic acid groups and preferentially release them. The result would be a reduction in the aspartic acid content of the material.

The histidine content of hide powder was reduced 50 per cent by the methylation treatment. Deaminization of the hide powder produced a material quite low in its lysine content. This reduction in lysine value from five per cent to one per cent in one day and to a half of a per cent in a week is in agreement with the results of Stubbings[1]. Prolonging the treatment beyond a day has also destroyed some of the arginine.

The color of the neutralized chrome leather hydrolyzate after centrifuging to remove colloidal chromium hydroxide was a pink to violet. This color was indicative of a chrome-amino acid complex. If any of the polar amino acids were involved in this complex, then the chromatographic behavior of this or these amino acids would be affected. This is because the chromatographic behavior of amino acids is related to the charges on their polar groups[23].

Since the chromatographic behavior of the polar amino acids in the chrome leather hydrolyzate did not differ significantly from that of the polar amino acids in an untanned hide powder hydrolyzate, one may presume the polar amino acids were not responsible for the chrome-amino acid complex and hence for the color of the chrome leather hydrolyzate. This does not imply that polar amino acid-chromium complexes are not formed during the chrome tanning process. The chromatographic behavior of the chrome leather hydrolyzate does indicate however that any such complexes were broken up by the conditions of hydrolysis.

There remains however the explanation for the pink to violet color of the neutralized chrome leather hydrolyzate. Küntzel and Riess[24] found that the neutral amino acid glycine reacted with basic chromium sulfate to yield a deep violet color. They obtained this same color by permitting a chrome sulfate solution to diffuse into a gelatin gel. In addition to verifying these results, it was found that a green basic chromium sulfate solution would give a violet color on reaction with any of the following: alanine, glutamic acid, aspartic acid, lysine, citric acid, ethanolamine, and diethylenetriamine. The amino acid reactions with the chrome are equilibrium reactions and are very much dependent upon concentration. The molar concentration of glycine per gram of collagen is one and a half times as great as the sum of the molar concentrations of the five polar amino acids discussed in this paper. Glycine in an amount equivalent to that occurring in one gram of collagen produces a strong violet color with the chrome, while a combination of the polar amino acids in the amounts they occur, produces only a very faint color under similar conditions. Since the polar amino acid analysis of the chrome sample did not differ significantly from that of hide powder it must be assumed that the reaction in the neutralized hydrolyzate between chrome and any of the polar amino acids did not proceed far, if at all.

The analysis of the material treated with trypsin under conditions normally used in the preparation of collagen shows that the polar amino acids are not attacked.

5. Summary

The quantitative analysis of the acidic amino acids of collagen, hide powder, and gelatin, using several methods, has been reported and some of the sources of error in these methods discussed. No difference was found in the dicarboxylic acid content of these materials by any of the methods or in their basic amino acid values as determined by chromatographic procedure. A method of analyzing for the dicarboxylic acids without separating them from each other is reported.

Modification of hide powder by nitrous acid treatment produced the expected low lysine value and by prolonging the treatment, arginine was also attacked. The aspartic acid value of a methylated hide powder was somewhat lower than that of untreated hide powder.

The analysis of formaldehyde and chrome tanned samples did not differ from that of untanned hide powder. Neutralization of the chrome hydrolyzate, followed by filtration, produced a deep rose to violet color in the filtrate. It is shown that the amino acid complex producing this color was formed during neutralization of the hydrolyzate rather than during the tanning of the hide powder.

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The Correlation Between Some Physical Properties of Leather

Part II. Data on Retan Leather*

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INTRODUCTION

In a previous paper[1] the correlation between some physical properties of Army retan side upper leather was considered. The interrelations of stitch tear strength, notch tear strength and grain crack strength 4 x 4 inch blocks from two entire sides were reported. The physical characteristics of the new location proposed in the revision of the military specification MIL-L-3122 of July 20, 1951 were also evaluated from the standpoint of the correlation which existed between tongue tear strength, stitch tear strength, tensile strength and small ball burst strength. It was found that there was interrelationship among the physical tests but that only half of the variance was accounted for in the inter-relations considered.

The location given in the military specification MIL-L-3122 of January 25, 1950 for physical test specimens was studied in this work on leathers received from various tanners of army retan leather. The leathers were from a different group of tanners of Army retan leathers than those who supplied the leathers on which the results in the first paper of this series were obtained. In addition to grain crack strength and stitch tear strength the samples submitted were also tested for tensile strength, total bursting strength, notch tear strength and tongue tear strength. Correlation among the physical properties would further emphasize whether two or more tests measured the same property and whether all were necessary to obtain a complete evaluation of the physical characteristics of the leathers.

EXPERIMENTAL

The specimens for test purposes were obtained from various lots submitted to this laboratory over a period of one year for compliance with MIL-L-3122. The samples varied from 7 to 16 as representative of any given lot of leather. All lots used in this work met the military specification MIL-L-3122 of January 25, 1950, on the basis of chemical analysis.

The number of samples used were as high as 600 pieces of leather for some tests in order to minimize the undesirable factors which occur with small

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TABLE I

The Correlation Between Some Physical Properties of Leather
Tabular Data are Sample Estimates of the Correlation Coefficients

Tanner	No. of Samples	Burst Strength vs. Grain Crack	No. of Samples	Tensile Strength vs. Notch Tear	No. of Samples	Burst Strength vs. Notch Tear	No. of Samples	Tongue Tear vs. Notch Tear	No. of Samples	Tensile Strength vs. Burst Strength
T	64	0.97	144	0.79	64	0.78	128	0.76	64	0.75
N	19	0.92	19	0.91	19	0.78	33	0.69	19	0.76
S	46	0.93	120	0.72	56	0.77	130	0.64	56	0.62
B	151	0.87	229	0.85	151	0.68	229	0.67	151	0.64
H	32	0.87	48	0.31	32	0.51	48	0.59	32	0.61
	Average value of the Correlation Coefficient (Z-weighting, Eliminating the Non-Significant Values).									
		0.89		0.83		0.71		0.68		0.67

Tanner	No. of Samples	Notch Tear vs. Grain Crack	No. of Samples	Tensile Strength vs. Grain Crack	No. of Samples	Burst Strength vs. Tongue Tear	No. of Samples	Stitch Tear vs. Tongue Tear	No. of Samples	Tensile Strength vs. Tongue Tear
T	64	0.75	64	0.70	64	0.66	128	0.70	128	0.65
N	19	0.76	19	0.74	19	0.36	33	0.64	19	0.63
S	83	0.71	73	0.59	56	0.58	130	0.61	120	0.51
B	212	0.58	212	0.58	151	0.62	229	0.53	229	0.57
H	32	0.50	32	0.54	32	0.45	48	0.45	48	0.49
	Average Value of the Correlation Coefficient (Z-weighting, Eliminating the Non-Significant Values).									
		0.64		0.61		0.60		0.59		0.55

Tanner	No. of Samples	Grain Crack vs. Stitch Tear	No. of Samples	Grain Crack vs. Tongue Tear	No. of Samples	Notch Tear vs. Stitch Tear	No. of Samples	Burst Strength vs. Stitch Tear	No. of Samples	Tensile Strength vs. Stitch Tear
T	128	0.70	64	0.67	144	0.71	64	0.71	144	0.65
N	33	0.64	19	0.47	33	0.63	19	0.44	19	0.75
S	130	0.61	83	0.58	130	0.47	56	0.36	120	0.47
B	229	0.53	212	0.46	229	0.46	151	0.52	229	0.46
H	48	0.45	32	0.39	48	0.35	33	0.33	48	0.11
	Average value of the Correlation Coefficient (Z-weighting, Eliminating the Non-Significant Values).									
		0.51		0.50		0.46		0.46		0.46

number of samples. The location of the samples submitted was one-sixth the distance from the root of the tail to the neckline, and one inch from the backbone edge, following the directions in the government specification KK-L-311.

After conditioning the tensile strength, tongue tear strength, notch tear strength and stitch tear strength were determined on the Scott tester. The grain crack and bursting strength were determined with the Mullen tester. From the results obtained the correlation coefficients between the physical tests were calculated to establish their inter-relation.

Results

In the first paper of this series [1] the meaning of correlation coefficients was given. When perfect correlation exists the correlation coefficient is equal to 1, which means that the values between two variables increase or decrease at a proportionate rate. When the value for the correlation coefficient is close to one, while correlation exists, it cannot be used as a good indicator of either property being compared.

Population Analysis and Corrected Correlation Coefficients

A population analysis was made of the data and the corrected correlation coefficients were calculated separately on each tanner's leather. This was done to establish whether the correlation coefficients of every tanners' leather were in the same population. In order to obtain the most significant results the irregular values in the respective data for each tanner were eliminated. The population analyses between the leathers were performed by means of the Chi-square test using the Z-weighting technique. [2] Then the corrected correlation coefficients were calculated. The results are shown in Table I.

Table I shows the correlation coefficients obtained on five different leathers and the fifteen different comparisons made. The leathers are coded as T, N, S, B, and H under the column marked tanner. The number of samples used to calculate the respective correlation coefficients of each tanner's leather as well as the correlation coefficients for each comparison is given. The average value of the correlation coefficient obtained by using the Z-weighting technique and eliminating the nonsignificant values is given at the bottom of each column for each comparison made. The table is also arranged so that the average value of the correlation coefficient for the respective inter-relations appear in decreasing order.

The first column shows the relation of bursting strength to grain crack strength and in the case of each tanner the leathers show good correlation for this comparison. The second column shows the correlation coefficients for each tanner's leather for the comparison of tensile strength versus notch tear strength. With the exception of the leather from tanner H their is fair correlation and the average value of the correlation coefficient after eliminating the non-significant values shows this to be the case. The small number of

samples from tanner N seemingly is sufficient to establish the inter-relation, and would be a sample for units up to 10000 according to KK-L-311. The larger number of samples further establish the reliability of the data.

There is also fair correlation in the comparisons of burst strength versus notch tear strength, tongue tear strength versus notch tear strength and tensile strength versus burst strength from the standpoint of statistics. While these are statistically significant correlations, taking the squares of the values indicated that less than 50 per cent of the variance is accounted for in their inter-relationships.

The leather from Tanner T shows reasonably good correlation coefficients in all inter-relationships while the leather from tanner H has about the lowest corelation coefficients in almost all of the inter-relationships. On the basis of chemical analysis both leathers met specification requirements and also those physical test requirements of the specification such as grain crack strength, stitch tear strength and shrinkage temperature.

When the irregular values of the data are eliminated the results show that all of the leathers from the tanners represented came from the same statistical population. It is also apparent that one tanner's leather can have much better correlation in all inter-relations considered than another.

Correlation Coefficients of all Inter-relations

A summary of the collected data of the correlation coefficients existing among the various inter-relations is given in Table II. The number of test values used for calculating each correlation coefficient is given in Table II on the left hand side of the table. The large number of samples used in some cases was possible because there was sufficient area on the samples submitted for the respective tests performed, while in other cases the samples were not large enough to permit all of the tests being conducted. Also some of the tanners only sent one or two lots during the year while others sent them in every month or oftener.

TABLE II

The Correlation Between Some Physical Properties of Leather
Tabular Data are Average Values of the Correlation Coefficients

Number of Samples Used for Each Inter-Relation — Left Side of Table
Correlation Coefficient of Each Inter-Relation — Right Side of Table

	Tensile Strength	Notch Tear	Burst Strength	Grain Crack	Tongue Tear	Stitch Tear
Tensile Strength	——	0.785	0.662	0.594	0.534	0.475
Notch Tear	639	——	0.708	0.644	0.670	0.512
Burst Strength	367	367	——	0.896	0.589	0.496
Grain Crack	479	503	357	——	0.465	0.393
Tongue Tear	623	668	367	503	——	0.575
Stitch Tear	639	702	367	503	686	——

The results of the calculations made on all of the samples tested are given in Table II on the right hand side of the table. The correlation of grain crack strength versus bursting strength is a fair correlation. It is a statistically significant correlation and taking the square of the correlation coefficient the value indicates that about 80 per cent of the variance is accounted for in their inter-relationship and the other 20 per cent of the variance is due to independent error sources.

When the correlation coefficients are squared for the other inter-relations less than 50 per cent of the variance is accounted for in the two properties compared in each instance. The data, while of a greater magnitude than that previously reported [1] gives values which are very similar in the respective comparisons which can be made. It also emphasizes that a single physical test would not measure all of the characteristics of the finish leather, with any degree of soundness.

Summary

On the basis of the data obtained in this research it is indicated that Army retan leather manufacturered by different tanners to meet the specification requirements of MIL-L-3122 of January 25, 1950 are all of the same statistical population. Some tanners produce Army retan leather which shows better inter-relations of physical properties than others.

While the data represents the physical properties of a different location on Army retan side leather than that used in the previous work, [1] similar values of correlation coefficients were obtained in the respective comparisons which could be made. The data emphasizes that grain crack strength and stitch tear strength, the two measurements required in the specification, will not necessarily reflect all of the strength characteristics of Army retan leather. Furthermore, while there is inter-relationship among the physical tests for the leathers used to obtain the data in this report less than half of the variance is accounted for in most of the inter-relations considered.

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A Test of Raccoon Skins for Suede Leather*

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Since World War II, there has been such a poor market for "long-haired" furs that many trappers have given up trapping altogether. Receiving houses for raw furs are overstocked with raccoon, opossum, skunk, fox, and coyote furs. These are still the "unwanted" furs, according to the trade designation. Because of this lack of demand for these furs, numerous attempts were made to find other uses for the skins. The idea that the lower grades of "long-haired" pelts might be tanned into some type of leather and sold at a profit, seemed logical. The Fish and Wildlife Service, Department of the Interior, was especially interested in an outlet for surplus raccoon skins because the trapping of these animals on the National Wildlife Refuges is necessary to keep them under control and thereby prevent excess depredation on waterfowl and upland game birds. The Bureau of Agricultural and Industrial Chemistry, Department of Agriculture, was interested in increasing the potential supply of leather, so a cooperative experiment was planned to determine the value of raccoon skins for suede leather.

The following general procedure was used for the test: (a) select approximately 500 average skins from animals trapped in the southern part of the United States, in a region where the quality of fur skins is normally low; (b) tan the skins into a suitable type of leather; (c) determine the cost of tanning; (d) market the skins, if possible, in order to establish their commercial value.

Skins for the test were obtained from the National and State Wildlife Refuges in Louisiana and Arkansas. Approximately 100 skins were obtained from each of the following locations: (for brevity, the lots will be referred to hereafter by the two-letter lot designation).

Lot WR—White River National Wildlife Refuge, St. Charles, Ark. (Peter J. Van Huizen, Manager).

Lot MI—Marsh Island and Grand Cheniere Island, La. (Armand P. Daspit, Director Fur and Refuge Div., La. Dept. of Wildlife and Fisheries).

*Credit is due R. M. Flaharty, now on military leave for assistance in this investigation.

**One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

Lot LS—Lacassine National Wildlife Refuge, Lake Arthur, La. (Charles M. Parker, Manager) and Sabine National Wildlife Refuge, Sulphur, La. (Vandiver L. Childs, Manager).

Lot MX—A mixed lot obtained from Lacassine and Sabine National Wildlife Refuges; Grand Cheniere and Marsh Island State Wildlife Refuges; and Vermilion Parish, Abbeville, La.

Lot DT—Delta National Wildlife Refuge, Pilottown, La. (Kent Meyers, Manager.)

At the Laboratory, the skins were numbered consecutively with a perforated die and weighed. The area was measured with a planimeter, and after the fur was clipped, the thickness of the skin was measured at a spot beside the backbone about 2 inches in front of the tail.

The skins were plumped with alum and G942 (a DuPont product)*, and then were chrome-tanned at a commercial tannery into black, suede, shoe upper leather. Suede leather, which is finished on the flesh side, seemed to be the best tannage for these skins because the grain or hair side of many skins was damaged by sores, scratches, scars, or similar faults, and they could have been finished on the grain, if at all, only after heavy buffing.

The tanned skins were graded at the tannery into three grades – C, D, and R (rejects). Later they were graded again by another sorter, with much the same results. Table I shows the grading data. Nearly one-third of the skins were classified as rejects, and a little more than one-half were just acceptable (Grade D). Relatively few of the skins had a good nap, i. e. ., a dense, even nap that did not show "bare" spots when the leather was stretched.

*In mentioning trade name in this publication, the Bureau of Agricultural and Industrial Chemistry, United States Department of Agriculture, does not in any way guarantee this product nor is it recommended in preference to others not mentioned.

TABLE I

Grade of Raccoon Leather

Grader	Source of skins	Proportion of skins in grade* C	D	R
		%	%	%
I	WR	10	63	27
	MI, LS, MX	6	73	21
	DT	0	37	63
	Average	6	63	31
II	WR	17	44	39
	MI, LS, MX	25	53	22
	DT	0	42	58
	Average	19	49	32

* C, fair; D, poor; R, reject.

Table II gives data on weight, area, and thickness for both the raw and tanned skins. The weight of the leather, based on the weight of the skins as received at the Laboratory, had the extremely low value of 17.8 per cent. There are several reasons for this great loss in weight. As a rule, the skins were greasy, and some had heavy deposits of fat on the flesh side; the hair comprised about 20 per cent of the weight of the raw skin, and in addition the hair of some pelts contained considerable dirt; and trimming out leather with tack or lacing holes and removing ears, snout, and claws caused appreciable loss in weight.

TABLE II

Weight, Area and Thickness of Raccoon Skins
and of Suede Leather Made From Them

Source of skins	Number of skins	Raw skins		Tanned skins	Yield Tanned/raw, %
		Range	Average	Average	
		WEIGHT — ounces			
WR	82	4.8 – 19.7	11.6	1.61	13.9
MI	92	2.5 – 18.4	8.4	1.49	17.7
LS	89	3.2 – 19.6	9.5	1.92	20.2
MX	97	3.4 – 18.4	9.0	1.76	19.6
DT	76	6.9 – 20.1	10.5	1.86	17.7
Average*	436	2.5 – 20.1	9.7	1.73	17.8
		AREA – square feet**			
WR		1.25 – 2.80	2.07	1.12	53.8
MI		.95 – 3.55	1.89	1.06	56.1
LS		1.20 – 3.10	2.11	1.26	59.7
MX		1.10 – 3.55	2.00	1.16	57.9
DT		1.45 – 3.15	2.16	1.38	64.0
Average*		.95 – 3.55	2.04	1.19	58.3
		THICKNESS – mils			
WR		21.6 – 93.7	53.9	29.4	54.5
MI		10.6 – 72.8	30.2	28.5	94.4
LS		12.6 – 68.9	30.1	30.5	101.1
MX		11.8 – 98.4	32.2	30.2	93.8
DT		17.7 – 74.8	36.8	29.1	79.1
Average*		10.6 – 98.4	34.5	29.6	85.7

* Averages except *total* for "Number of skins" and *Maximum spread* for "Range".

** Area of raw skins was measured through the tack or lacing holes because it would be necessary to trim the skins inside this line during tanning. The recorded areas are, therefore, less than those of the original skins, and the area yields are slightly high.

The loss in area (42 per cent) was less than the loss in weight (82 per cent)* nevertheless, the decrease in area from an average of 2 square feet per skin in the raw state to hardly more than 1 square foot after tanning was a serious loss. Since such leather is sold by the square foot, the possible selling value was only a little more than half of what it would have been if there had been no shrinkage. In the second place, the reduction in size made economical cutting impossible. The thickness of a skin varies from backbone to flanks and from head to tail, so that it is difficult to cut pieces of reasonable uniformity from such small skins. Plumping during tanning was at least partly responsible for the decrease in area, yet it was not effective in developing a satisfactory nap.

In general, the loss in weight, area, and thickness during tanning, together with the poor nap, made use of the skins for shoe leather impractical. Another type of leather might have given somewhat different results; however, no other type seemed to offer more promise of successful use. One of the first uses suggested was for glove leather, but a glove manufacturer stated that he could not use such small skins because the costs would be prohibitive. The skins seemed to have no unusual qualities that would make them particularly suitable for some special type of leather.

The physical and chemical properties of 16 tanned skins, selected as representative of the trapping areas and of the skins in size and quality, were determined. The results are given in Tables III and IV. Tensile strength (Table III) was satisfactory for this type of leather. The data indicate that as quality decreased there were an increase in area yield, and decreases in weight yield, tensile strength in the direction parallel to the backbone and in stretch in the perpendicular direction. The data, however, are too meagre for definite conclusions.

The chemical analyses (Table IV) do not reveal any differences that may be ascribed to source of skins or quality of leather. In fact, the composition is not unusual and is uniform between skins.

A number of shoe firms and wholesalers were approached regarding purchase of the leather. None were interested. The pieces were small and, therefore, would be expensive to cut into shoe parts; also the nap was poor, so that the leather would be suitable only for low-quality shoes. If nap quality had been excellent, the skins could have been used in spite of their small size. On the other hand, if they had averaged 4 or 5 square feet in area they could have been used even though the nap was poor. Sale of a small lot of leather—only about 500 square feet—would be difficult, however, under any circumstances.

An estimate of the value of the raccoon leather, at a season when suede was not in demand, was 10 cents per square foot. Later, when the demand

*Part of the difference between area shrinkage and weight shrinkage is due to the fact that the trimmed area, rather than the full area, of the raw skins was measured. See footnote 2, Table II.

TABLE III

Physical Properties of Raccoon Leathers

Skin No.	Source of skins	Leather grade	Weight yield %	Area yield %	Density oz./cu. in.	Tensile Strength lb./in.2*	Tensile Strength lb./in.2**	Stretch * %	Stretch ** %
1	WR	C	18	58	0.38	5,730	3,060	32	102
2	WR	D	13	47	.35	4,890	3,160	32	84
3	WR	R	15	57	.36	5,360	3,230	32	86
4	WR	R	13	60	.35	4,420	2,460	26	75
5	MI	C	14	42	.36	6,200	3,200	28	78
6	MI	D	20	49	.35	4,990	2,620	30	106
7	MI	R	13	62	.33	4,120	3,160	32	65
8	LS	C	23	52	.36	6,000	3,680	30	82
9	LS	D	19	44	.34	5,480	2,990	29	81
10	LS	D	24	60	.33	5,490	2,860	28	87
11	LS	R	16	64	.34	5,760	3,460	32	72
12	MX	C	20	46	.32	5,390	2,730	30	78
13	DT	D	17	54	.33	4,940	2,360	28	62
14	DT	D	17	59	.34	4,940	2,720	22	74
15	DT	R	15	60	.34	4,860	2,530	35	76
16	DT	R	21	60	.32	4,040	2,090	24	58
Average			17	55	.34	5,163	2,894	29	79

* Parallel to backbone.
** Perpendicular to backbone.

TABLE IV

Chemical Analyses of Raccoon Leathers

Skin No.	Source of skins	Hide substance N x 5.62	Fat (petroleum ether extract)	Ash	Chromic oxide (Cr_2O_3)
		%	%	%	%
1, 2	WR	76.5	5.9	3.6	2.8
3,4	WR	74.1	6.5	3.7	2.7
5, 6, 7	MI	74.7	6.1	3.7	2.7
8, 9	LS	75.2	5.6	3.7	2.7
10, 11	LS	76.5	5.1	3.8	2.8
13, 14	DT	76.1	5.7	3.7	2.7
15, 16	DT	75.3	5.3	4.0	2.8
Average		75.5	5.7	3.7	2.7

for suede was good, an estimated value of 15-18 cents per square foot was placed on it but even 18 cents would not quite cover the cost of tanning. It does not appear that the leather would sell for enough to pay for tanning it, under any circumstances.

If use of the skin for leather had proved feasible, the fur would have been a by-product. Hair or fur removed by the usual tannery wet process has relatively little value, being suitable only for use in insulation or padding. A possible, more important use appeared to be for making felt. A hat manufacturer examined a few samples and found the fur satisfactory for hat felt. He estimated it would be worth approximately 1 dollar a pound.

For felt, the fur must be clipped, because that removed by a depilitant does not felt satisfactorily. In the present method of clipping fur for felt, the skin is reduced to shreds which have no value for making leather. A machine has been designed to clip whole skins, but it damages the skins so that they cannot be used for leather. Nineteen machine-clipped skins yielded 17.1 ounces of fur. As the fur would be worth less than 6 cents per skin, it would not pay the cost of trapping the animals. An average of 2 ounces of fur per skin was obtained with small, hand-operated, electric clippers, but the operation was too slow for commercial use. Salvage of the fur, either with or without use of the skin, does not appear economically feasible under present conditions.

SUMMARY

Long-haired furs have not been in demand since World War II, and a large surplus has accumulated. To determine the possibility of using such skins for leather, 500 raccoon skins were tanned commercially to suede, shoe upper leather. The tanned skins were small and the quality of the leather was poor. A typical comment of a shoe manufacturer was the following: "The leather appears to have sufficient strength and weight for shoe purposes but would be extremely costly to cut because of the small size of the skins. The nap is not comparable to good suede, being sparse and having a tendency to open up, which we believe would not make a very attractive shoe."

Raccoon skins could not be tanned profitably to suede leather, and tanning to other types of leather does not appear any more promising. Salvaging the fur for felt would yield little profit, if any.

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ABSTRACTS

Vegetable Tanning Materials of Poland. By T. Bodalski. *Compt. rend. med. acad. polon. sci.*, pg. 12 (1949). Through *C.A.* **46**, 9875 (1952). The raw materials, characteristic reactions, and methods for the determination of tannin, as well as results of researches on Polish vegetable tannins, are described. Varying results were obtained according to the type of raw material. *Cortex quercus*, *C. salicis*, *C. piceae*, *C. alni*, and *Rhizoma bistortae*, *R. Tormentillae*, and *Folia uvae ursi*, were studied and their tannin contents determined. New raw materials were examined, i.e., a tannin-producing plant from Altai, *Bergenia crassifolia* (family *Saxifragaceae)*, and gall nuts growing on *Quercus pedunculata*, after injection of *Cynips kollari:* the latter contain 14 per cent of tannin, and resemble the Turkish gall

nuts *(Gallae turticae)* containing 32.2 per cent of tannin. An enzyme found in gall nuts decomposes tannin, producing ellagic acid. The ellegic acid content of the raw material, determined by an enzymic method, is about 7 per cent. The tannin content of the rhizomes of *Bergenia crassifolia* cultivated in Poland, was 21.58 per cent by the Cu and 22.4 per cent by the Sn method; previous values were 24-26 per cent.

Aquatic Organisms as an Aid in Solving Waste Disposal Problems. By R. Patrick. *Sew. and Ind. Wastes* **25,** 210 (1953). The various ways in which aquatic organisms may be of use in solving problems associated with waste disposal are discussed. There are commonly five ways in which wastes may harm the aquatic life of a river, as follows: 1. They may produce oxygen deficiency. This may be due to the bacteria, which attack the wastes and use oxygen in their metabolic processes. The wastes also may not be completely oxidized when they are discharged and thus take up oxygen from the water in completing the oxidation necessary to stabilize them. 2. They may be toxic to aquatic life. This may be due to the nature of the chemicals themselves. However, it may be due to the pH which they create in the river. Wastes also may be toxic due to osmotic pressure which they develop in river water, thus bringing about conditions unfavorable for aquatic life. 3. Temperature changes produced by wastes may be harmful in two ways. The amount of change which they produce may be deleterious. It is a well known fact that a sudden change in temperature of more than two degrees is harmful to the sunfish. Also, a waste, by raising or lowering the temperature of a river only two degrees, may cause the temperature of the water to be in a critical range deleterious to the functioning of certain physiological processes necessary for life. 4. The physical properties of the waste may be harmful. They may carry suspended solids that are abrasive and thus injure mechanically the membrane of the gills of fish. In other cases, such as oil, they may coat the gill structures and thus make the absorption of oxygen from the water impossible. 5. Wastes may render the habitats of aquatic organisms untenable. For instance, suspended solids may settle out and clog up the natural habitats of aquatic organisms. Eggs may become buried. In other cases the added pressure created by settleable solids may cause the egg cases to burst. Some wastes produce turbidity, thus hindering light penetration. Thus the photosynthetic zone of a river will be greatly restricted and the algal production limited. The author describes briefly two methods for studying the effects of pollution: laboratory tests and river surveys. Realizing the importance of the biodynamic cycle, the effect of a given waste is determined in the laboratory tests by using organisms representing three stages in the cycle namely: an alga, an invertebrate (snails and insects) and fish. Such tests are acute toxicity tests. It is hoped to develop chronic toxicity tests also. Laboratory toxicity tests are of value to industry in solving the following types of problems: 1. In planning a waste disposal unit. 2. In changing a process of treatment. 3. In installing new types of waste treatment. 4. When dumping settling basins at high river flow, to determine how much can be dumped at a given flow without damaging aquatic life. 5. When an industry is accused of causing a given damage and there are other effluents emptying into the river, to determine whether or not the accused industry is to blame. In a river survey all of the organisms established in a given region of the river are identified as to species. The chemical characteristics of the water are determined. A total bacterial count and a coliform count are made, and the B.O.D.'s are determined. A histogram is then made of each region studied. From the pattern developed by the columns of the histogram, the state of the "health" of a river is determined. One of the great values of this type of study is that it tells the condition in the river over a period of time. Because these aquatic organisms have life histories of varying lengths, one is able by examining the structure of the population to determine when in the past a deleterious effect occurred. This type of study is of value to an industry just starting operations as it

will define the condition of the stream without their wastes. This method also is useful in determining whether a waste treatment program is sufficient to protect the river. If an industry is accused of damaging a river, such a survey, comparing various sections of a river, can tell if the complaint is justified. Both the laboratory toxicity tests and the biological surveys are valuable aids in defining the pollution problem. J. F. W.

The Influence of Chromium Compounds on Activities of a Sewage Treatment Plant. By R. Vryburg. *Chemisch Weekblad* **48,** 689 (1952). Through *Sew. and Ind. Wastes* **25,** 240 (1953). Mixed sewage and industrial wastes containing 259 ppm. chromium compounds (as Cr) caused difficulties in a treatment plant. The settled fresh sludge contained 0.4 per cent Cr on a dry basis; the primary digestion tank sludge, 1.2 per cent; the secondary digestor sludge, 2.0 per cent; the humus in the trickling filters, 2.8 per cent; and the final settling tank sludge, 1 per cent. Laboratory experiments showed that gas production was reduced by one-half with 500 ppm. Cr. and to one-sixth with 1000 ppm. Cr.

Slaughterhouse Waste Digestion. By W. Rudolfs and V. Del Quercio. *Water & Sewage Works* **100,** 60 (1953). Digestion of slaughterhouse waste can be accomplished to any desired degree in upflow digesters by controlling the rate of feeding. B.O.D. reductions of 95 to 98 per cent are readily attainable with relatively low loadings. Both volume and B.O.D. loadings must be considered for best results. About one month should be allowed to acclimatize the inoculum for optimum performance. Drastic mixing may result in deterioration of the effluent and loss of seed sludge. Acclimatized seed sludge withstands shock loads without difficulty. Upflow digesters produce better results than "batch" digesters.

The Composition and Reactivity of Collagen. By J. H. Bowes. *Abstracts Communs., First Inter. Congr. Biochem.,* pg. 129 (1949). Through *C.A.* **46,** 6419 (1952). The minimum molecular weight of ox hide collagen, as calculated from amino acid analysis, is 39,000. It contains chondrosamine, glucosamine, 0.33 per cent hexosamine, and probably chondroitin sulfate. Nitric acid converts NH_2 groups to OH groups almost completely, and causes a loss of 20 per cent of the arginine. The COOH groups are esterfied when the collagen is treated with methyl sulfate or methyl bromide. The esters are stable at pH 2-8. Some *N*- methylation may occur, especially with methyl bromide. Formaldehyde appears to react mainly with amino and guanidino groups. Tannings with chrome or vegetable tannins depends on coordination or electric charge, respectively.

Reaction of Gelatin with Mineral Tanning Agents. By A. Popova and A. G. Pasynskii. *Zhur. Priklad. Khim.* **25,** 18 (1952). Through *C.A.* **46,** 6420 (1952). The method of calculating the extent of binding of a tannin by the substrate by the determination of deviation of the titration curves of the mixtures from additive curves of individual components was applied to chrome alum and alum. The results are given graphically. The isoelectric point of the protein is shifted from 5 to 3.8 by alum and 3.95 by chrome alum. Titrations in the acid region reveal almost no binding but titration with alkali reveals considerable binding. At pH 8-10 it reaches 3.8-4 or more millemoles per gram.

The Suitability of the Internal Membranes of Dead Animals for Tanning and Their Disinfection Prior to Handling. By O. Roemmele. *Tierärztl. Umschau* **4,** 10 (1949). Through *C.A.* **46,** 7804 (1952). Experiments are reported on the preservation and tanning of the following tissues: pericardium, Pleura, peritoneum, the yellow skin of the

abdomen, the yellow mucous membrane of the first stomach, the fascia transversa, the bladder of the ox, horse and hog, and the gold beaters skin of the cecum of the ox. These tissues were very resistant to putrefaction. They were best preserved by soaking 24 hours in concentrated brine and then dry salting. The tissues must be freed from fat, flesh, and connective tissue. For complete sterilization they were soaked for 24 hours in one per cent formic acid containing 0.02 per cent mercuric chloride, then one hour in concentrated brine, and then drained. After 24 hours the membranes were sterile and even mold spores were destroyed. No difficulties were encountered in the chrome tanning of these membranes.

Rhus Typhina as a Potential Source of Domestic Tannins. By J. Vahala. *Sbornik Ceskoslov. Akad. Zemedelske* **24,** 377 (1951). Through *C.A.* **46,** 7805 (1952). Results of cultivation of *Rhus typhina* in various parts of Europe are reviewed. Experimental cultivation on a small scale has been done for several past years in Czechoslovakia. Small scale tanning experiments from leaves were inconclusive; better results were obtained for upper leather than for sole leather. In both cases a combination with other tanning materials is recommended. Tannins from *Rhus typhina* are cheaper than those from spruce bark and much cheaper than synthetic tanning materials.

The Preparation of Photographic Gelatin from Hides. By D. R. Dhingra, M. G. Gupta and M. C. Bhattacharya. *J. Proc. Inst. Chemists* **23,** 161 (1951). Through *C.A.* **46,** 8401 (1952). The desired properties of photographic gelatin are well established, but methods for preparing it have not been published. The following procedure yielded a product said to compare favorably with commercial gelatins. Dehair calf skin by the usual liming procedure, wash; delime with 2 per cent H_2SO_4; wash free from acid; cut into pieces and cook 3 times with 3 volumes of distilled water; combine the extracts; bleach with SO_2; clarify by filtration and centrifugation; concentrate to 20-25 per cent in vacuuo at 45-50°; add 0.004 per cent HCHO; after solidifying in a refrigerator slice and dry in a stream of air at 25-28°. Yields were 35 to 44 per cent on the dry limed weight. The product contained H_2O 13.6 and ash 2.32 per cent (consisting of SiO_2 4.6, Al_2O_3 2.8, Fe_2O_3 0.4, P_2O_5 8.3, CaO 54.4, MgO 11.3, Cl 1.05, SO_3 19.3 per cent); pH value (2.5 per cent solution) 6.8; water absorption 1200 per cent; viscosity (2.5 per cent solution) 1.58 (water = 1); setting point (15 per cent solution) 18°.

Determination of the Density of Leather. By G. D'Orsi. *Cuois, pelli, mat. concianti* **28,** 35, 93, 156 (1952). Through *C.A.* **46,** 8403 (1952). The methods of determining the density of leather and other solid materials are: (1) direct measurement of volume and weight; (2) determination of volume by mercury displacement; (3) displacement of a liquid other than mercury; (4) displacement of a gas. The last named method is the most exact. A new method and apparatus is suggested which permits the determination of density, with gas displacement on either leather or hide powder. The average values obtained were: vegetable tanned leather 1.535, hide powder 1.602, raw dry hide 1.715 - 1.735.

Notes on Tannin Analysis by the Filter Method. By U. Lubrano and G. Falanga. *Cuoio, pelli. mat. concianti* **28,** 205 (1952). Through *C.A.* **46,** 8403 (1952). Comparative analyses of various tanning extracts made with filter bells of different dimensions and different amounts of hide powder (chromed, French, Batch EFT/5) show that the apparent nontannin content increases with the amount of hide powder and with the height of the hide powder column in the bell. The differences are lower for chestnut extract and higher for sumac and sweetened extracts. No differences in residue weight were found with different dehydrating compounds in the desiccators (such as $CaCl_2$, H_2SO_4, silica gel).

Evaluation of Some Vegetable Tanning Materials. By G. W. Schultz. *Lea. and Shoes* **125,** No. 5, 8 (1953). Since the official method of Tannin Analysis does not accurately reflect the tanning value of the material under examination, the author has devised another procedure which is described as follows: two solutions of the tanning material are made up on the official basis of 60 grams tannin per liter. One of these is adjusted to pH 4.4, corresponding to the iso-ionic point of hide substance. The idea back of this is that below pH 4.4 acid substances will combine with hide, and above this point basic substances should combine with it. Therefore any combination occurring at the isoelectric point must be that of the true tannins. Ten grams of hide powder are soaked over night in 100 ml. of water. Then 6 grams of tannin in 100 ml. of water added, and the whole shaken intermittently over a 24-hour period. This is done with both natural and pH-adjusted solutions. In order to check the effects of volume and concentration, the author also used solutions of double volume, and 33 per cent greater concentration, respectively. The results are shown in the following table:

Per cent Tannin Taken Up By 10 Grams of Hide from

	6 g. in 200 ml. solution		12 g. in 400 ml. solution		12 g. in 300 ml. solution	
	Orig. pH	pH 4.4	Orig. pH	pH 4.4	Orig. pH	pH 4.4
Myrobalams	91.7	74.2	73.6	58.0	73.3	60.8
Mangrove Bark	89.1	86.3	75.0	69.2	76.1	72.9
Wattle Bark	88.3	95.0	65.0	72.9	69.0	77.5
Quebracho Ext.	85.0	85.0	67.6	66.7	70.7	70.7
Divi Divi	81.3	72.5	68.8	61.7	68.2	60.8
Chestnut Ext.	76.0	64.1	59.3	45.8	61.3	48.8
Lignin Ext.	54.1	42.1	20.9	20.0	20.0	18.8

At the natural pH, the tanning materials classify from best take-up to the poorest in the order shown in the first column but, on pH adjustment, wattle bark goes into first place, and myrobalams shift to the fourth position. In fact, all acid tanning materials, with a pH lower than 4.4, dropped materially in take-up when their solutions were adjusted to pH 4.4. This drop is attributed to the elimination of acid absorption, and the variation in results on the original solutions in the case of acid materials is caused by the amount and probably the kind of acid present in the several materials. While the author used quebracho, chestnut and lignin extracts, the other materials were represented by leach liquors. Regular extracts of the latter usually give lower values than those reported in the table. The extent of the drop is measurably affected by the treatment of the liquors during their concentration. Bisulfited quebracho is affected by the amount of bisulfite used and the manner of bisulfiting. Lignin extract is not regarded as a tanning material, and its take-up by hide is looked upon as due to acid combination analogous to the acid take-up in the cases of tanning materials cited above.

Semichrome Gloving Leather from East India Leathers. By M. Bannerjee. *Tanner* **6,** No. 3, 21 (1951). Madras tanned sheep and goat skins are dipped in water, piled over night, shaved the following morning, and weighed. They are stripped by drumming for an hour in 2 per cent borax and 500 per cent water, the borax solution run off and the stock washed well with cold water. For the chrome retanning, a 33 per cent basic solution is used. Two per cent Cr_2O_3 on the shaved weight is added to the stock in the drum in three portions at hour intervals. Tanning is complete in 4-5 hours, when the stock should stand

the boiling test. Stock is horsed up over night, neutralized the following morning with one per cent borax, then washed with 2-3 changes of water. It is then dyed with an acid dye, usually 1-2 per cent dye on the shaved weight, and the dye developed with formic acid. Stock is then fatliquored with 5-6 per cent neatsfoot oil, 1-2 per cent fish or castor oil, and 1-1.5 per cent soft soap for 45 minutes at 50°C. Stock is struck out, dried for a few days, then put down over night in damp sawdust staked the following day, tacked out to dry, and subsequently finished. The finish consists of 5 parts pigment finish paste, 5 parts Bedacryl 188 A, 1/4 part acid dye, 1/4 part Turkey red oil and 75 parts water. The bottom coat is put on by brush, the second coat by brush or spray. A 3 per cent formaldehyde solution is finally sprayed on and the stock dried. A nitrocellulose lacquer may be sprayed on to produce resistance to wet rubbing.

Our Hides and Skins. By S. Raja. *Tanner* **6,** No. 6, 14, No. 7, 16 (1951). This is a very well illustrated article. The 24 cuts show the manner of collection, cure, selection, trim, drying, brining and baling. Census of livestock and data on export of raw hides and skins and tanned stock are given. Description of Pakistan hides and skins and their markings are given in some detail.

The South Indian Tan-Wattles. *Tanner* **6,** No. 7, 19 (1951). An outline of the difficulties encountered in the establishment of wattle groves in India. It has been found that the wattle does best when protected by Eucalyptus plantings. The Eucalyptus should be planted 40 feet apart, and the wattle twelve. It is recommended that large scale wattle plantings continue on grasslands as heretofore, but that Eucalyptus shelter be established well in advance.

Wattle. *Tanner* **6,** No. 7, 22 (1951). Wattle was introduced into India about 1840 to provide cheap fuel for the Army stationed at Wellington. In South India, latitude 8-11 degrees north, wattle does well at elevations above 5,000 feet. It can grow on a wide variety of soils, but does best on deep, well-drained soil. A temperature range from 85°F. in summer and 40°F. in winter is most suitable. It cannot stand severe summer nor temperatures below 30°F. The most suitable rainfall is 35-70 inches per annum. Plantings may be by seed or seedlings, in well prepared soil. Grass seriously impedes growth. Fertilization with manure is highly beneficial. During the first two years the plantations must be carefully weeded. Young plants are easily killed by frosts. Bark is stripped from the grown tree from the trunk upwards to one inch in diameter, and is spread out on brush or poles to dry with the outer surface uppermost. If the under surface is exposed to the sun a bad discoloration results.

Investigation on the Course of Protein Hydrolysis in Wet Salted Hide During Storage. By B. N. Pal and P. K. Sarkar. *Tanner* **6,** No. 10, 15 (1952). Freshly flayed hide was washed free from blood and dirt, then well salted, and stored for a period of four months. During this period, the hide was sampled at six intervals, and moisture, hide substance and dissolved hide substance determined. Moisture increased from 46.55 to 55.1 per cent in the first two weeks, but thereafter decreased to 39.5 per cent at the end of four months. Hide substance, dry basis, decreased from 96.15 to 70.5 per cent in the same time. Dissolved hide substance increased from 0.40 per cent to 1.78 per cent during the storage period. It was determined by shaking the hide with water for two hours, and analyzing the water for nitrogen. Hide slip was noted after one month's storage, and at the end of the

four months the flesh side was slimy and the salt red. The authors state that analysis of hide for soluble proteins can serve as a means of detecting putrafactive hydrolysis, and the increase in percentage of soluble proteins serve as a measure of the progress of the putrefaction.

Warble—Cause of Great Economic Loss. By R. Bahadur. *Tanner* **6,** No. 11, 13 (1952). Hypoderma lineatum and Hypoderma Crossi are both found in India. The first species attacks cattle and the latter attacks goats. Cattle of the districts of Ferozpore and Sargoda in the Punjab and the northeastern part of the United Provinces and goats of northwestern Punjab, Northwest Frontier Province, Sind, Baluchistan, United Provinces, Rajputana, western Bihar and Orissa are warble infested. About 80 per cent of the goatskins of Sind, United Provinces, Orissa and Western Bihar have warble marks and holes. Bihar goatskins, known as Tirhoots, which are collected in the goatskin market at Muzzafarpore are showing 50 per cent of the summer supply and 30 per cent of the winter supply to be warble damaged. The warble pest is spreading and is now reported in West Bengal. It is reported that about 75 per cent of the goatskins exported from Calcutta show warble damage. It is recommended that steps be taken to combat the warble pest.

Chemico-Physical Interpretation of Hides and Skins. By M. Bannerjee. *Tanner* **6,** No. 10, 19, No. 11, 21, No. 12, 14 (1952). A general article dealing with the chemical and physical composition and structure of animal skin.

Plastics and Their Applications in the Leather Industry. By J. K. De. *Tanner* **6,** No. 12, 23, 7, No. 1, 26, No. 2, 24 (1952). After giving a general description of plastics the author states that plastics can be used for finishing leather, for impregnating leather to improve its substance, tensile strength, waterproofness, and abrasion resistance. They may be used in any of the following ways: (1) In aqueous solution of monomers or precondensates. (2) As emulsions of intermediate polymers. (3) As solutions of polymers in organic solvents. (4) As monomers in organic solvents. (5) In solution of polymerizable solvents. The first two are the most popular methods of application. Methacrylate resins are extremely useful in the finishing of leather. They are self plasticizers, are flexible, and produce elastic films. They adhere well to leather and are particularly useful for defective grains which have been corrected by light snuffing. Polyvinylacetonaphthalate is capable of emulsifying nitrocellulose with water and such emulsions are rapidly gaining in favor. Impregnation of leather with plastics gives fuller substance, tightening of loose parts, increased abrasion resistance, and waterproofness. Impregnation with monomers and subsequent polymerization has not proved successful. Rubber latex cannot penetrate leather, but emulsions of synthetic plastics and rubber can be prepared with sufficiently small particle size to permit their being drummed into leather. This treatment may temporarily increase waterproofness but has no filling effect. Acrylic resins and polyvinyls are used as cementing materials in leather board manufacture. They are also used in shoe factories to replace rubber latex and rubber cement. Thermo setting plastics, without modification, are unsuitable for finishing leather. The phthalicanhydride-glycerol polymer can be modified by replacing a part of the anhydride with a monobasic fatty acid, whereby a product is obtained which is softer and soluble in common solvents. It is gradually finding use in leather finishes with or without the addition of pigments. Impregnation of leather with thermo setting plastics has not attained any importance except in the case of "Resol". Here leather is impregnated with phenol and formaldehyde, and after some reaction, any excess is washed out. Solubilized plastics in the form of syntans have long been used in tannins. A

new form of the phenolformaldehyde syntan is under investigation as a tanning agent. Two mols of phenol are reacted with 3 mols of formaldehyde at 70°C. for 2-3 hours, caustic soda acting as the catalyst. The resultant syrupy liquid contains some unreacted constituents which are removed. The condensate can be used for tanning at pH 8, but the leather is thin and tinny. The fullness and feel of the leather are improved and fixation of the tanning agent considerably increased by acidification. On standing, the condensate tends to become insoluble by further aggregation of the molecules.

Leather Research. By M. B. Das. *Tanner* **7**, No. 1, 12, No. 2, 13 (1952). A lecture stressing the importance of histological, microscopical, bacteriological and chemical research on hide, examination of tanning materials, and research on tanning processes and leather.

An Investigation Into the Indigenous Tanning Materials of India. By P. K. Sarkar. *Tanner* **7**, No. 1, 17, No. 3, 15, No. 4, 15, No. 5, 15 (1952). The Indian Government has made a survey of indigenous tanning materials, as follows: (1) haritaki fruits (Terminalia Chebula); (2) haritaki bark (Terminalia Ekebula); (3) sonalu bark (Cassia Fistula); (4) khair heartwood (Acacia Catechu); (5) babul fruits (Acacia arabica); (7) matgoran bark (Ceriops roxburghiana); (8) small goran bark (Ceriops candolleana); (9) sundri bark (Heritiera Minor); (10) dhemdal bark (Carapa obovata). (11) keora bark (Sonneratia apelata); (12) passur bark (Cerapa Moluccensis); (13) garjan bark (Rhizaphore acutangula); (14) hopea bark (Hopea parviflora). The materials were analyzed by the J.S.L.T.C. method and extraction was by the Procter extractor.

Limed light cowhide was delimed with boric acid and tanned in liquors from the various tanning materials. Stock was in a 1 per cent tan liquor for 1 day, then in a 2 per cent liquor for a day, and in a 4 per cent liquor for seven days, after which it was suspended in water for 5 minutes, blotted, oiled on grain and dried for analysis.

In the data which follow, tanning material is numbered according to numbers in the first paragraph, its analysis is on 10 per cent moisture basis, and resultant leather is on 14 per cent moisture basis. (1) tannin 28.22, soluble nontans 24.45, sugar 5.21, pH 5.0, tannin group--pyrogallol. Suitable for making solid myrobalam extract. Leather, hide substance 48.04, water solubles 5.26, C.T. 30.57, D.T. 63.63, yield 40.4, Character, soft, full but somewhat spongy, color yellow. (2) Tannin group-pyrogallol. Tannin 39.63, soluble nontans 5.95, sugar 4.83, pH 5.2. Highly astringent. Leather, hide substance 38.21, water solubles 9.93, C.T. 35.47, D.T. 92.83, yield 38.1. Character, moderately soft, strong, noncracking, but flat and lacking substance. Penetration somewhat slow, color, light brown. (3) Tannin group-catechol. Tannin 12.62, soluble nontans 6.29, sugar 1.84, pH 5.1. Suitable for light skins. Leather, hide substance 47.04, water soluble 6.81, C.T. 30.36, D.T. 64.54, yield 47.4. Character, pinkish color, soft and pliable. (4) Tannin group-catechol. Tannin 6.63, soluble nontans 5.54, sugar 1.67, pH 5.5. Suitable only for extract manufacture due to low tannin content of liquor. Leather, hide substance 54.67, water solubles 8.08, C.T. 20.77, D.T. 37.99. Character, leather strong. (5) Tannin group-mixed pyrogallol and catechol. Tannin 5.81, soluble nontans 4.94, sugar trace, pH 5.0. Very poor in tannin so of no commercial value. Leather was hard, bony and undertanned. (6) Tannin group-catechol. Tannin 10.36, soluble nontans 7.30, sugar 1.60, pH 4.5. Leather, hide substance 42.91, water solubles 8.69, C.T. 31.95, D.T. 74.46. Character, soft, noncracking. Tanning material suitable for commercial tanneries and is used to some extent. (7) Tannin group-catechol. Tannin 20.81, soluble nontans 10.28, sugar 0.29, pH 4.5. Quite good mangrove, suitable for heavy and light leathers. Leather, hide substance 49.04, water solubles 6.71, C.T. 28.82, D.T. 58.80. Character, strong, tight, reddish brown in color. (8) Tannin group-catechol.

Tannin 20.27, soluble nontans 8.50, sugar 0.25, pH 5.5. Quite good mangrove, suitable for heavy leather and extract, the latter containing more than 50 per cent tan. Leather, hide substance 49.05, water solubles 6.88, C.T. 28.54, D.T. 58.19. Character, reddish brown color, soft, strong, tight grained. (9) Tannin group-catechol. Tannin 8.70, soluble nontans 5.20, sugar trace, pH 5.0. Not suitable for large scale tannings. Leather, hide substance 49.81, water solubles 7.64, C.T. 25.30 D.T. 50.79. Character, harsh and brittle, very dark red in color. (10) Tannin group-catechol. Tannin 28.65, soluble nontans 7.06, sugar 7.06, pH 5.5. Liquor is highly astringent and must be blended with less astringent tannins. Leather, hide substance 52.25, water solubles 1.61, C.T. 30.60, D.T. 58.56. Character, cracks badly, harsh, dark red color. (11) Tannin group-pyrogallol. Tannin 10.63, soluble nontans 9.40, sugar 0.48, pH 6.0. Not suitable for extract because of high nontannin content. Leather, hide substance 51.37, water solubles 5.41, C.T. 26.65, D.T. 51.90. Character, harsh, hard, cracky, red brown in color. (12) Tannin group-catechol, Tannin 12.20, soluble nontans 3.94, sugar 0.12, pH 6.0. Suitable for sole and dressing leathers. Good for extract. Leather, hide substance 54.46, water solubles 8.39, C.T. 21.91, D.T. 40.23. Character, pliable, tight grain, light red in color. (13) Tannin group-mixed pyrogallol and catechol. Tannin 14.44 soluble nontans 8.65, sugar 0.08, pH 5.5. Leather, hide substance 49.41, water solubles 3.16, C.T. 30.98, D.T. 62.70. Character, good strength, noncracking, red colored. (14) Tannin group-catechol. Tannin 14.38, soluble nontans 6.41, sugar 0.80, pH 4.5. Suitable for extracts, deserving commercial exploitation. Leather, hide substance 39.67, water solubles 5.83, C.T. 33.02, D.T. 83.24. Character, soft, strong, full, good color.

Chemistry of Oil Tannage. By P. K. Sarkar. *Tanner* **7,** No. 3, 23 (1952). A short review of the chemistry of oil tannage as expressed by Fahrion, Meunier, Chambard and Michallet.

Treatment of Industrial Wastes. By M. M. Luckens. *Lea. Mfg.* **63,** No. 7, 7 (1952). A general discussion of the subject.

Simplified Construction of Experimental Tanning Drum. By J. T. Hernon. *Lea. Mfg.* **63,** No. 7, 7 (1952). Detailed description with dimensions of an experimental tanning drum.

Special Questions from Gluing Practice. By E. Plath. *Holztech.* **29,** 191 (1949). Through *C.A.* **46,** 9334 (1952). The adhesiveness of a glue depends on the resistance to shear, the molecular forces, and the forces of adhesion. Principles to be observed in the application of glues are discussed.

Boiling (Thermal Shrinkage) of Dry Collagen. By G. I. Kutyanin. *Doklady Akad.* Nauk. *U.S.S.R.* **82,** 405 (1952). Through *C.A.* **46,** 9878 (1952). The initial shrink temperature of dermal collagen in H_2O can be regarded as an index of thermal stability of dehydrated leather or skin, which depends at least in part on cross-linkages introduced in the tanning process. Dry collagen, either tanned or untanned, is capable of such shrinkage on heating. Hydrated untanned collagen shrinks at about 70°, while completely dehydrated specimens shrink at about 210° or higher. Leather specimens kept under a slight load (5 g.) were heated by means of a Wood's metal bath, and the dimensional change was measured. The results, given graphically, show that a contraction to 82-6 per cent of initial length occurs (terminal readings). The untanned or oak-tanned hydrated specimens shrink

precipitously at 70-80°, while chrome-tanned hydrated specimens shrink similarly at about 120°. The dehydrated forms (tanned or untanned) shrink rapidly by 6-8 per cent in the 120-240° interval and show a very steep shrinkage at about 210-40°. At higher temperatures a slight length increase occurs, owing to plastic flow under load. Hence, tanning as such does not affect the thermal stability of dry collagen and merely produces cross-links that affect hydrothermal stability. Very likely relatively few links of this type are formed per mol. unit. The water-dependent linkages between mol. fibers are probably H bonds or electrovalent links between chemically active portions of the mols. The shrinkage temperature of collagen is similar to the softening temperature of other high polymers, while the effects of hydration on the properties of collagen resemble the effects of plasticizers on other high polymers.

Casein Glues. By H. Hadert. *Farbe. u. Lack* **50,** 67 (1950). Through *C.A.* **46,** 9878 (1952). The optimum properties of casein for glue manufacture and the factors influencing them are discussed in some detail. The main requirement is fresh, i.e., odorless and non-fatty, casein. It should dissolve easily in alkali to give a clear solution. (This property depends on drying temperature during manufacture) and should have a certain ash value (depending on requirements), which determines the viscosity (n) of the glue and is high for acid-processed casein. Casein is definitely acidic and forms well-buffered solutions; those of low n give the best glues. Formulas for powdered glues by using $Ca(OH)_2$ with a Na salt or a hydrolyzing Na salt alone, and for various cold glues, are given together with hints on their stabilization and n control.

Adhesives. I. Hen Egg White. By Y. Sumiki and S. Matsushima. *J. Agr. Chem. Soc. Japan* **22,** 127 (1949). Through *C.A.* **46,** 9878 (1952). Hen egg white powder was obtained by (a) drying the coagulate formed by heating the raw egg white with HCl at 70°, (b) drying the coagulate formed by adding EtOH to the raw egg white, (c) freezing and drying the coagulate formed by warming 30 minutes at 68°, and (d) drying the coagulate formed by heating the filtrate from the coagulate of (c) at 70° at pH 4.7. These products were mixed with $Ca(OH)_2$, NaOH, NaF, and H_2O. The adhesive strengths of the glues made from (a) to (d), respectively, were 22.0, 35.0, 37.0, and 25.5 kg./sq. cm. The control glues from casein and from soybean protein had adhesive strengths of 74.8 and 43.0 kg./sq. cm., respectively. Riboflavin could be recovered by adsorbing on acid clay from the filtrate from the coagulated egg white. The riboflavin content of the filtrate was 98.5-102.8 kg. whole egg.

Influence of the Conditions Under Which Chrome Tannage Is Carried Out on Its Duration and on the Distribution of the Chrome Through the Thickness of the Leather. By P. S. Briggs. *Premier Congres International. Union Int. des Socs. de Chim. des Ind. du Cuir.*, pg. 56, Sept. 1949. The advantages of the use of iso-electric skin, both from the point of view of the laboratory and the tanner, are pointed out; not only are the changes which take place more easily comprehended but the progress of tannage becomes less susceptible to variations in liquor/stock ratio. The studies were made with iso-electric skin and using (a) a large liquor/stock ratio so that, although a usual concentration of chrome (1.75 per cent) was used, the concentration did not change appreciably and (b) a relatively small (50 per cent to 200 per cent and also 500 per cent) liquor/stock ratio so that the initial concentration of chrome (1.75 per cent) changed during the course of tannage. In both cases, liquors of 33 per cent, 42 per cent and 50 per cent basicity were used. (a) Samples of hide were taken after 7 hours, 24 hours and 18 days. After removing the excess

liquor, the samples were aged 48 hours, washed to remove excess chrome and then split into 5 layers. If the chrome content of the dicerent layers be x_1 x_2, x_3 — x_5 and their mean be $\bar{x}$, the standard deviation with respect to the mean is $S^2 = \frac{\Sigma (x - \bar{x})^2}{n - 1}$ and the "coefficient of variation" is $\left(\frac{s}{\bar{x}} \times 100\right)$ per cent and it is believed that, where many results are involved, this coefficient is better adapted for their rapid assessment. Due to locational variations, in work of this kind from any one series one can only draw conclusions which are restricted to that series. The coefficient of variation for 33 per cent basic liquor levels off at 10 per cent at the end of 4 hours; the coefficient for both 42 per cent and 50 per cent basic liquors is about double that of the 33 per cent liquor in the early stages but by the end of 7 hours, all three show approximately the same value, and all reach their minimum when the chrome content of the leather is in the range of 3.5-4.5 per cent. At lower percentages of chrome, the 33 per cent basic liquor gives a more uniform distribution. When per cent chrome is plotted against time, the grain layer shows a single convex curve which indicates that basicity modifications of the tanning complex are not of importance. However, in the middle layer, whereas the curve for the 33 per cent basicity is still convex, that for the 42 per cent and 50 per cent basicity is concave and the two curves only come together after 7 hours tannage. The balance between diffusion and combination, between the physical and chemical properties of the chrome complex must be considered when dealing with heavy leathers. (b) Samples of hide were taken after 24 hours tannage, washed to remove soluble chrome and then split into 5 layers. As the basicity increases, exhaustion liquor becomes less sensitive to variations in liquor/hide ratio. However, the chrome content of the leather showed a maximum at a liquor/stock ratio of 1/1 for liquors of 33 per cent and 42 per cent basicity; at 50 per cent basicity a similar value was found at a liquor/hide ratio of ½/1, the chrome fixed decreasing as the ratio increased. Analysis of the grain and median layers showed that, despite the similarity in the total chrome fixed, the layer-wise distribution varied according to the basicity. The less basic liquors showing more uniform distribution whereas, in the more basic liquors, fixation was much greater in the grain than in the centre. The important effects of distribution on the character of the leather and its behaviour during splitting and shaving in the blue are indicated. When the "Coefficient of Variation" is plotted against liquor/hide ratio, it is seen that basicities of 33 per cent to 42 per cent and liquor/hide of 50 per cent to 100 per cent give leathers containing 4-4.8 per cent chrome in the grain and 2.5 per cent to 3.5 per cent in the middle thus producing, within reasonable working hours, a large variety of types and feel of leather, all of which, starting from iso-electric hide, are suitable from the commercial viewpoint. The effects of phthalates and formates, as masking agents, are considered. Small additions of phthalate (1/3 mole sodium phthalate per 1 mole Cr_2O_3) speed up tannage and give well-filled and solid leather. However, analyses of the layers does not show more uniform distribution of the chrome and the use of higher quantities of phthalate leads to the formation of large particles so that penetration is restricted. With formates, the results are rather different. At 33 per cent basicity, 1 mole formate increases the chrome content of the leather and lowers the coefficient of variation from 24 per cent to 18 per cent; the use of 2 moles shows no changes in the chrome content or distribution; with 3 moles, the coefficient of variation is lowered to 8 per cent but the leather contains somewhat less chrome. At 42 per cent basicity, all the additions of formate modify the chrome distribution but reduce the chrome content. All leathers, of both basicities stand boiling. With 50 per cent basicity, 1 mole produces no change in chrome content or distribution but the leather shrinks @ 99°C; 3 moles formate produce no change in chrome content but the coefficient of variation is reduced from 50 per cent to 20 per cent, placing it on a par with all except one of the series. Hence, with formates, both the basicity and degree of masking are of importance. A.N.K.

Zirconium Tannage. By M. Paquet. *Premier Congres International.. Union Int. des Socs. de Chim. des Ind. du Cuir,* pg. 137, Sept., 1949. Zirconium tannage started in Europe around 1935 and used the oxychloride in the presence of sulfates. The tanning liquors obtained had a pH of 0.6 - 0.7, and a basicity of about 50° Sch. This was too high and was reduced with acid and so resulted in even lower pH's. Not only was the leather yellowish, due to changes in the hide, but the liquors were extremely corrosive. Too, the oxychloride was costly. Hence the process was not successful. In 1941, in the U.S.A., the basic sulfate of Zr was used with success. With this salt, the pH was 0.9 - 1.0, still very low but better than with the oxychloride. The leather from the iron-free sulfate was perfectly white, the process was as simple as Cr tannage. However, on thick hides, the grain and flesh fixed too much ZrO_2 while the centre remained too acid. Hence the process was only suitable for lighter leathers. Even so the process was costly both because of the expense of the zirconium sulfate and because about twice as much ZrO_2 was required as was needed of Cr in Cr-tannage. Studies were therefore made to overcome these defects. The first problem was to produce a cheaper Zr salt, using the raw materials available in Europe viz: zirconia or zirconium silicate. The silicate was purified by physical methods and calcined with alkali. The product was converted directly into tanning compounds by causing it to react with conc. H_2SO_4 (or mixture of acids) in the presence of water vapor. Under these conditions, the silica was converted into silica-gel which retained water enough to allow complete conversion of the mixture. Since the reaction is carried out in the solid phase, the product is immediately ready for use after cooling and grinding. During the process, additions can conveniently be made to improve the tanning power. The product obtained is a white powder, containing 16-20 per cent ZrO_2 and having the properties, which can be adjusted by suitable changes in the process, necessary for Zr tannage. In practice, the Zr compound dissolves slowly in the water (the slowness being regulatable by the manufacturing procedure). The silica gel remains insoluble but it absorbs the Zr compounds and only releases them to the bath as they are absorbed therefrom. Hence it is not "inert", though readily removed from the skins during the washing after tannage. *Characteristics of Zr tanned leathers:* the leather is perfectly white throughout the thickness, and is very full. The quantity of ZrO_2 fixed is about 2.2 times the amount of Cr_2O_3 fixed in Cr tannage. Based on the drained pickled weight, between 4.5 and 5.5 per cent is used but this may be increased to 8-10 per cent for firm and thick leathers. The shrink temperature is usually 94-96°C. Tensile strength and tear resistance are slightly poorer than Cr leathers of equal thickness, though Zr tannage gives a thicker leather than does Cr. The color is light-fast, if non-oxidizing oils are used in fat-liquoring. The leather is easily washed, especially if sulphonated fatty alcohols are used. Washing with alkaline soaps is not advised as the leather becomes less resistant to tearing. The leather dyes easily to give clear, solid colors. *General Considerations:* In agreement with the work of Somerville and of Schakowsky, the authors find the optimum pH for tannage to be between 1.6 and 2.4, with basicities of 25-40° Sch. To obtain these conditions, Zr complexes must be used. It is also suggested that there are at least three kinds of Zr tannage: (1) that obtained at pH values below 1.0, giving shrink temperatures of 88-90°C. (2) that obtained with Zr complexes with optimum at pH 1.6-2.4 and shrink temperatures of 94-98°C. (3) that obtained with colloidal hydrated ZrO_2 with an optimum at pH 5.5-6.0 and shrink temperature of 82-83°C. In ordinary practice, all 3 types co-exist. For the proper tannage of heavy hides it is necessary to reduce the reactivity of the tanning solutions and also reduce their colloidal nature in order to avoid the dialyzing effect which results in poor penetration. These objectives were studied. It is said that the normal and basic Zr sulfates are actually zirconyl-sulfuric acids of the formula $ZrO(SO_4)_y H_x$ in which "x" and "y" depend on the conditions. Soluble zirconyl sulfates form complexes with soluble sulfates and these are less colloidal than sulfates of Zr, thus penetrating better. Acidocomplexes behave similarly. Chlorides favor the forma-

tion of the colloidal basic Zr sulfate and can be used to initiate fixation when the pH is low. The tanning compound fixed by the hide seems, in all cases, to be a basic sulfate insoluble in the acids present in the bath or skin. While the composition is not certain, it seems to be 1 mole ZrO_2 with 0.45 - 0.55 mole of $SO_3 + H_2SO_4$. For proper fixation and shrink temperatures, the pH must be slowly raised: this is best achieved by the use of buffer salts. Neutralization is completed at about pH 4.5 by the use of $NaHCO_3$ or, in the case of light leathers, by merely washing with water. Suggested formulae are given for pickling and tanning of different types of skins and hides, and it is pointed out that, for heavy hides, NaCl in the pickle should be avoided being replaced by sulfates, especially those of Na, Mg or Al. For fixation of the tannage, after penetration is complete, buffer salts may be used; these, being expensive in Europe, can be advantageously replaced by the use of MgO, using one-sixth of the total ZrO_2. This brings the pH to 2.6 - 2.8. Then add 2 per cent Al sulfate to bring the pH to 3.8. Washing should be thorough, first in running water and then for 20-30 minutes with 100 per cent luke warm water (20° - 30°C) containing 1 per cent of sulfonated fatty alcohol. Drying should be done carefully in order that the Zr colloids may be transformed slowly: in the first stage, the stock should be brought slowly to a temperature not exceeding 28 - 30°C. with air of high relative humidity; the second stage is conducted as is usual for vegetable tanned stock. Zr leathers generally require 2-4 per cent of oil and it is pointed out that, for white leathers, the newer materials which do not yellow are best. A good mixture is: mineral oil—2; sulfonated oil for white leather—1.5; neatsfoot oil—0.6; sulfonated laurylalcohol—0.6 (percentages on wrung weight). Wetting agents, by lowering surface tension, are valuable not only in washing but also in the actual tanning and sulfonated alkylnaphthalenes have been found most suitable. Iron, vegetable and some synthetic tannins readily stain these white leathers and wooden drums rarely give a pure white until 3 or 4 packs have been processed. Chrome also stains but is less serious; indeed, where a blueish or greenish white is wanted, small quantities of basic Cr sulfate may be added to the tanning bath. Zr tannages give very supple full leathers and can be applied to all sorts of skins, either alone or in combination with other tannages. For the smoothest leathers, the basicity (Sch) should be reduced by adding acid; the chlorides should be reduced and replaced by sulfates, (esp. those of Na or Mg) or by bisulfates. For grained leathers, the basicity should be increased at the start of the tannage to about 50° Sch and using chlorides in the pickle. For glove leathers, use only 3 per cent ZrO_2 (instead of 5 per cent) and a suitable fatliquor. For firm leathers, the ZrO_2 is increased up to 8-10 per cent. A rapid control method for determining the ZrO_2 content of the bath consists in transforming the sulfates into chlorides with $BaCl_2$/HCl and then titrating with a known solution of NaF, using as indicator a solution of 2/1000 of sodium alizarin sulfonate mixed with tincture of indigo. Details will be given in subsequent papers. To follow the rate of penetration, a piece of stock is cut off and placed in cold water for five minutes, when the progress can be determined by observing the cut edge. By placing a few drops of a solution of 1/1000 of alizarin sulfonate on the cut, the ZrO_2 distribution can be seen in a few minutes. A. N. K.

Contribution to the Study of Tannage with Zirconium Sulfate. By R. Lasserre, *Premier Congres International. Union Int. des Socs. de Chim. des Ind. du Cuir*, pg. 126, Sept. 1949. In earlier studies, tannage had been carried out on pieces of parchment (at pH - 5) with pure solutions of zirconium sulfate of increasing concentration and it had been found that while the amount of both Zr and SO_3 increased therewith, their ratio remained constant. Since the pH of the solutions was less than pH-1, the skin swelled enormously so that, in a second series, Na_2SO_4 was added in increasing amount. These additions while lowering the fixation slightly, did not change the ratio. Using pickled skin of varying acidity, there

was a slight drop in Zr fixed and a drop in the ratio ZrO_2/SO_3 absorbed by the pelt. Continued washing of the tanned pelt with water removed the acid without affecting the Zr fixed so it was supposed that zirconium tannage was due to the Zr ions and not to a zirconium sulfuric acid complex. Tannage of deaminized pelt, and pelt which had had the amino-groups blocked by HCHO, gave the same results. Hence fixation could not occur at the amino groups. During the above tests, it was found that a sulfato-zirconium complex was fixed and the ratio ZrO_2/SO_3 was 0.835, whatever the basicity, using isoelectric pelt, but the ratio varied with pH. In the above, also, the ratio of ZrO_2/SO_3 in the bath remained constant. In the present work, studies of basicification were made, using NaOH, Na_2CO_3 and $Zr(OH)_4$. As in the case of chrome liquors the basicity was expressed in

$$°Sch = \frac{ZrO_2 \text{ basic} \times 100}{ZrO_2 \text{ Total}}.$$

The total ZrO_2 is obtained by pptn. with ammonia and ignition @ 900°C. Combined ZrO_2 was determined by the method of Procter & McCandlish. Basicities of 0° - 60° Sch were prepared in steps of 10° Sch, using solutions of 2.5 per cent ZrO_2. With N/1 NaOH, the ppt. dissolved slowly and at 60° Sch only after standing overnight. With Na_2CO_3 (10 per cent), the ppt. dissolved readily. With either NaOH or Na_2CO_3, increasing amounts of Na_2SO_4 were formed so another set was prepared in which Na_2SO_4 was maintained constant. Finally a series was prepared using freshly pptd. $Zr(OH)_4$. This would only dissolve on heating. On standing, all deposited crystals except that at 60° Sch with $Zr(OH)_4$ which became opalescent. The crystals were examined under the microscope and two types were observed: (1) Pure zirconium sulfate at 0° Sch, and those made basic with $Zr(OH)_4$, produced biaxial prismatic needles, weakly birefringent and mono- or triclinic. They correspond to those reported by Falinski as having the formula $7\ ZrO_2 \cdot 5\ SO_3 \cdot 30\ H_2O$. (2) Basicification with NaOH or Na_2CO_3 and zirconium sulfate (0° Sch) with added Na_2SO_4 produced hexagonal prisms whose ends were truncated into six-sided pyramids. These were different from those of Na_2SO_4. While the composition of these is still being studied, it was observed that Na_2SO_4 retards their appearance and that basicity has little bearing on their formation. Tannage was also carried out on pieces of parchment using 5 per cent ZrO_2 on pelt weight and 200 per cent water and of basicity varied from 0° to 60° with Na_2CO_3 and with the Na_2SO_4 maintained constant. The tanned skin was washed twice for one-half hour each. At 60° Sch, flocculation occurred immediately. ZrO_2; SO_3, free or combined with ZrO_2; and Na_2SO_4 were determined in the residual baths and wash waters. Swelling was determined on the wet leather. On the dry leather, ash; ZrO_2; SO_3 hide substance; and the ratio of ZrO_2/SO_3 absorbed were determined. (1) Fixation of ZrO_2 increased slowly with basicity to 30° Sch and then fell rapidly. (2) Minimum swelling (max. index of dehydration) occurred at 30° Sch. (3) While the ratio ZrO_2/SO_3 in the baths varied from 0.77 to 1.54 at basicities of from 0° to 50° Sch, that of the leather varied only from 1.28 to 1.54, corresponding to basicities of 40° to 50°. At 50° Sch, the ratio ZrO_2/SO_3 was the same for the pelt and the bath, and fixation was weakest. It is supposed that above 40° Sch a different type of tannage occurs. Since basicity seems to play such a minor role, studies were made of boiled and unboiled solutions of the tanning liquors by means of ion-exchange resins. The results indicate that the latter solutions contain the normal ionized salt whereas the former contain only 14 per cent of the Zr as the normal salt and the rest as either anionic or not charged. Due to the low pH and the character of the resin, further differentiation was impossible. However, tannage with both kinds of liquor gave identical results. Since amino-groups were not the active centers of tannage, tannage was carried out on pieces of skin which had been methylated (Me_2SO_4; MeOH + Ac_2O; Me_2SO_4 + Na_2CO_3 to repress swelling). The methylated skins were divided into three sets. One was used to determine the degree of methylation while the remaining two were tanned with 5 per cent Cr_2O_3 or ZrO_2 respectively, using chrome alum of 30° basicity and pure $ZrSO_4$. Comparison tannages were made on skin not methylated. Compared with the con-

trols, there was a distinct difference in the appearance of the chrome tanned methylated pelt; the color being greenish black and with little fiber separation. In the case of zirconium tannage there was very little difference. Analysis of the leather indicated that methylation reduced the Cr_2O_3 fixation by 20-30 per cent; ZrO_2 fixation was little affected and, since the CH_3 content remained constant, no demethylation had occurred. From this it seems as if fixation is not through the carboxyl groups. Studies were made of neutralization at pH values from 2 to 10. The tanned stock was rinsed twice before neutralization. $NaHCO_3$ was used for neutralizing to pH - 5 and Na_2CO_3 for the higher pH values, the pieces were rinsed twice and dried. Above pH - 8 swelling became large and wringing and washing difficult. Also, the presence of Zr and of hide substance was observed in the baths. From the data ZrO_2 fixed remains constant to pH 7.5 - 8 and then drops with breakdown of the skin. SO_4 falls from the start and reaches zero at pH - 6.2. Resistance to hydrolysis is a maximum at pH 5 while resistance to dehydration is a maximum at pH 4.5. The leathers were difficult to wet-back, especially at pH 4.5 to 5. It would seem as if a certain quantity of SO_4 ions is necessary for the best tannage. In conclusion, it is felt that zirconium tannage differs from that of chrome by the pH at which it is carried out, as well as (1) fixation of ZrO_2 remains the same whether the solution is completely ionized or whether it contains non-cationic complexes: (2) basicification has little influence on the tannage: (3) neither de-amination nor partial blockage of the carboxyl groups affects the fixation of ZnO_2 and it is suggested that tannage takes place by coordination with the peptide links. A. N. K.

The Present Situation of the Synthetic Tannins. By Dr. Siedermann. *Premier Congres International. Union Int. des Socs. de Chim. des Ind. du Cuir.*, Pg. 100, 1949. The history of the Syntans is divided into two portions: (1) 1911-1930 (2) 1930 to date. During the first period, that of the auxiliary syntans, Neradol D of Stiasny was the type. These were obtained by condensation of cresol-, or phenol-, sulfonic acid with HCHO. Due to the characteristics of such condensation, the product is a mixture of many molecular weights and that is of some advantage. While increasing the mean molecular weight, by increasing the proportion of HCHO, increased the tanning power up to a certain maximum, further increases resulted in a falling-off in the tanning powers. As produced, the products are too acid and must be neutralized to avoid harmful swelling of the pelt. However, since their tanning power mainly centers in the reaction between their sulfonic groups and the amino-groups of the hide, complete neutralization destroys it. The use of naphthalene-sulfonic acids was tried but these products were of lower tanning power due mainly to the difficulty of a degree of condensation corresponding to the maximum tanning power. Though etherification of the phenolic hydroxyl groups only feebly weakens sthe tanning power of the cresol/phenol syntans, the absence of such hydroxyl groups adversely affects the tanning power of the naphthalene syntans. The use of other aldehydes and also of ketones was tried in order to modify the tanning power of these syntans but the products had only weak tanning powers. However, the reaction between urea and HCHO was of interest as it gave tannages of good solidity and light (fastness). Due to their low tanning power, the auxiliary syntans are little used today in the actual tannage but they are useful both as solubilizing agents for certain vegetable tannins, as speeding diffusion and as mordants during dyeing. About 1930 the replacement syntans appeared. These can be divided into 2 main groups: (1) those of I.G. based on phenolic or polyphenolic resins (2) those, of Geigy, based on on dioxydiphenylsulfone. The first type is produced by first forming the phenol-HCHO resin. During this condensation a mixture of more or less large phenolic chains is produced. However, the composition of the mixture and the degree of condensation can be controlled according to the conditions of the reaction. The resulting resins are then sulfonated. With this type of syntan, the tanning power centers around the hydroxy groups and, in general, sulfonation is a minimum for

solubility. These syntans therefore have high tanning power and are fully dispersed with the aid of auxiliary syntans, such as the products of the condensation of naphthalene sulfonic acid and HCHO. Increased tanning power of this type of syntan is obtained by using poly-hydroxyphenols instead of phenol. Another way of increasing the tanning power is by increasing the acidity of the phenolic OH. For this purpose dioxidiphenylsulfone was used and results in an increased tanning power. Also, this grouping readily combines with a great many aromatic sulfonic acids so that, by varying these, the relative proportions of the components, and the conditions of reaction, an unlimited number of products with differing properties can be produced. In this type of syntan, the aromatic sulfonic acids play the same role as does sulfuric acid in the simple phenolic tannins so that the tanning power varies inversily as the content of aromatic sulfonic acids. Basically, then, the tannnig power of these syntans is influenced by the same factors as governs that of the monophenolic tannins, except that the phenolic groups are more reactive. The similarity between the natural and the replacement tannins as to their behavior with gelatine and salts, as well as the similarity of their leathers is indicated. A.N.K.

Quality Control and the Analysis of Synthetic Tans. By U. J. Thuau. *Premier Congres International. Union Int. des Socs. de Chim. des Ind. du Cuir.*, pg. 109, Sept. 1949 Those synthetic tannins which have tanning powers equal to those of the vegetable tannin are acido-complexes of synthetic resins (phenol-; cresol-; urea-; etc.—formaldehyde, or mixtures of these) usually dispersed in the sulfonic acids of phenol, cresol, naphthalene, or other hydrocarbons, or in mixtures of these acids. To these, buffer salts must be added. Previously it had been shown that tannage with these materials is a resinification and that such materials only tan if combined with, preferably, an organic acid as an acido-complex. Since synthetic tannins are different from natural tannins, why should the same method of analysis be applied—chrome, iron or zirconium materials not being so evaluated. The following outline for evaluation is suggested: (a) an actual tanning test, on hide, and measuring shrinkage on drying; (b) total solids; (c) soluble solids; (d) total mineral matter; (e) official tannin analysis; (f) content of synhtetic resins, and of hydrocarbons from the sulfonic acids, where these are used as dispersing agents; (g) SO_3 combined with organic matter (sulfonic acids); (h) total SO_3, including sulfates; (i) urea content; (j) ammonium salts; (k) qualitative tests on the composition of the resin and of the sulfonic acids; (l) pH and acidity; (m) organic acids and their nature; (n) shrink temperature of leather tanned in (a); (o) other. Details are given as to the methods for suitable tannage (a) and shrinkage should not exceed 10 per cent. For b and c, the official methods are used. Under (d), a five gram sample is dissolved in water, filtered and washed. The insoluble portion is ashed and dissolved in HCl. Both extracts are made to volume and analyzed (separately) both qualitatively and quantitatively. Under (e), direct detannization, with E.F.T.D. hide powder, is carried out. Except in the presence of ammonium salts, the tannin is very closely the difference between soluble solids and mineral matter. With ammonia present, it must be calculated to the sulfate. The difference ("tannin") corresponds to the resins and organic acids added to form acido-complexes. Under (f), 50 ml. of a 10 per cent solution is treated with 50 ml. of HCl (22°/Be'), shaken until foaming ceases and refluxed on the water bath for 1 hour. If the material which separates is solid, it is filtered through a tared filter, washed with hot distilled water, dried and weighed; if liquid, a separating funnel is used and the material dissolved in a suitable solvent and washed in another funnel with a solvent suitable for the resin or hydrocarbon present (benzene, $CHCl_3$, ether, etc.). This is evaporated in a tared flask, etc. This value is most important. Under (g), it is pointed out that acid hydrolysis at atmospheric pressure, as in (f), does not give a complete breakdown. It is suggested that the determination be made in two stages: (1) SO_3 in the filtrate

and washings obtained in (f) and (2) SO_3 remaining in the recovered resins, etc. For this (1), the filtrate, etc., is neutralized to pH 6, 5 gms. Na_2O_2 is added and the whole boiled for one-half hour. Then acidified with HCl and precipitate with $BaCl_2$. Or, (1 b) one can use benzidine hydrocloride which combines to give sulfate and the alkyl-sulphate; the latter being soluble in hot EtOH, the two types of sulfate can be separated. A 2 per cent or 3 per cent benzidine hydrochloride is prepared in the cold and stored in brown glass bottles. Twenty ml. of the solution to be tested is neutralized to pH 7 with NaOH in an Erlenmeyer flask, adjusted to pH 5.2 with N/1 HCl and then add 10 ml. of the benzidine solution. The mixture is vigorously shaken and then allowed to settle. Filter and wash three times, each with 10 ml. of distilled water. The filter and ppt. are placed in another erlenmeyer and 60 ml. of 95 per cent EtOH added and boiled for several minutes. Filter hot, washing the flask four times, each with 10 ml. of hot 95 per cent EtOH. The alcoholic filtrate, which contains the alkyl sulfates, is diluted with water, acidified with HCl and SO_3 determined by pptn. with $BaCl_2$ as usual. (2) SO_3 remaining combined with resins, etc., is determined by mixing the washed, dried, and weighed residue on the filter in (f) with two parts of Na_2CO_3 and one part $NaNO_3$ and fusing. The melt is dissolved in distilled water, acidified with HCl and SO_3 obtained by pptn. with $BaCl_2$. Under (h) (total SO_3, including sulfates) five or 10 g. of the tannin is diluted with 50 per cent of its weight of water and, with stirring, sufficient Na_2CO_3 is added slowly to bring about pH 7. Then add, with constant stirring, five g. Na_2O_2, heat and boil gently for one-half hour. Cool, acidify and precipitate SO_3 with $BaCl_2$. The ppt. corresponds to the total SO_3. Sulfates are determined by gentle ashing of the neutralized tannin followed by solution of the ash in water and HCl and precipitation with $BaCl_2$. This last is not exact as some of the sulfonic acids are transformed into sulfates during the ashing. Urea (i) is determined by Kjeldahling the resins collected from the acid hydrolysis (f) and calculating the ammonia recovered to urea. Ammonium salts (j) are determined by Kjeldahling the original material and deducting the ammonia found in (i). The qualitative examination of the components of the synthetic resins and of the sulfonic acid hydrocarbons (k) is listed. (a) phenol and cresol. To five ml. of a 1 per cent solution of the syntan on a watch glass, add some 40° Be′ caustic soda, followed by a few drops of 5 per cent potassium ferricyanide. In the presence of phenol or cresol, a deep red color is obtained. Or, by heating the resin with alcoholic KOH mixed with p-nitraniline, a red color is obtained. By progressive oxidation with sulfochromic and acetic acids, cresol resins yield CO_2 and water. (b) Urea, determined as in (i). (c) Naphthalene—2 to 3 drops of a 1 per cent solution of syntan are mixed with as many drops of 3 per cent H_2O_2, followed by 2 ml. of conc. H_2SO_4 and mix. In the presence of naphthalene, a blue-violet color develops. (l) pH and acidity are determined by the glass electrode and the acidity calculated both as SO_3 and acetic or formic acids, according as the one or other predominates. (m) Organic acid content and study of these acids. (1) Distill 100 g. of 10 per cent syntan until volume reduced to 30 ml. Cool and add 70 ml. H_2O and redistill. Repeat four times. Titrate the distillate with N/1 NaOH and calculate both as acetic and formic acids. (2) Same as (1) but using steam distillation. If ammonia passes over, it can be determined by Kjeldahl. (n) Any well known shrink-temperature apparatus suitable. (o) Of other studies, that of the behavior on mixing with vegetable tannins is of importance. However, even if it precipitates with vegetable tans, it could be of interest as a fixing agent for heavy vegetable leather. A.N.K.

"Experimental Studies on Valonias from Turkey, Greece and Palestine." By O. Gerngross. *Premier Congres International. Union Int. des Socs. de Chim. des Ind. du Cuir.*, pg. 98, Sept. 1949. By studying the cups from different trees and different areas of Greece and Turkey, six main types were recognized: Type I with a beard which surrounds

the cup like a cuirass; type II with a beard "shredded" and curvey; type III with the beard very thick and curved backwards almost into loops; types IV and V which have a flower-like appearance; type VI which is distinguished by its size and by a "forest-like" beard on the upper part of the cup. The first three types were the most common in all regions visited. A given tree always produces the same type of cup and its tannin content is quite constant from year to year. Type II tends to be lower in tannin (34 per cent) than the other five varieties (31-38 per cent with a max of 46 per cent—shake method of analyses). Grecian samples while good, tended to be somewhat lower in tannin, but no samples were found to give the low values of 14-20 per cent reported in the literature. In Palestine, the situation is different: a great many kinds and varieties, of varying tannin content, were found. 15-20 per cent tannin is far from rare, though 30 per cent and upwards was found in some localities. Palestine valonias, especially the rich types, unlike those of Greece and Turkey are characterized by a smaller quantity of beard. Analyses were made of the different portions of cups, and a table is given showing the variation in tannin content of the different parts, together with the percentage they form of the whole. Thus, in the example given, the tips of the beard represented 28.05 per cent of the whole and contained 56.42 per cent tannin; at the other extreme, the innermost layer of th cups represented 11.42 per cent of the whole and showed 17.52 per cent tannin. The overall analysis of the sample showed 46 per cent tannin. While their studies are not complete, it is felt that the tannins of the different parts of the cup are of different qualities and that this has bearing on the phytophysiological role played by tannin in the plant. The standards set up by the Commission of Standardization at Symrna are based on (1) degree of purity, (2) color, (3) size, (4) density. However the studies show that, while purity and clear color are signs of good quality, size has no bearing on the richness in tannin; indeed, often the reverse. The relationship between density and tannin content is still felt to be uncertain. A.N.K.

Iron Tannage. By C. Gastellu. *Premier Congres International. Union int. des Socs. de Chim. des Ind. du Cuir.* pg. 72, Sept. 1949. In general, all processes for tannage with iron can be classified into three main groups: (1) Those which use relatively simple salts such as chloride, sulfate or acetate of iron. (2) Those in which the inorganic or organic complex salts of iron are used. (3) Those in which one or other of the above are used in combination with another tannage, such as chrome, formaldehyde or syntan, and satisfactory leather has only been obtained by methods of the second and third groups. As a result of the studies made since 1941, it is now known why the earlier attempts failed and what conditions must be observed to obtain a satisfactory tannage. The earlier attempts all started with salts of group 1 and such salts are much more strongly hydrolyzed than the corresponding chrome salts, giving rise to solutions of much lower pH. As with chrome, a true leather cannot be produced if the final pH is much below an optimum (for chrome, pH 3.5 to 4; for iron about pH 3). However, due to the instability of the iron salts, one cannot attain such a pH; futher, pelt placed in solutions of these simple salts swells but does not tan, and if very concentrated solutions are used, or the swelling is restricted by use of neutral salts, all that is achieved is a sort of pickling and the "leather" will not resist washing nor is its shrink temperature much above that of untanned pelt. However, by adding to the solutions substances which have the ability to form complexes with iron, the hydrolysis can be decreased and the stability of the solutions increased so that suitable iron salts can be produced. Of the various substances tested, tartaric, adipic and, particularly, phthalic acids produced iron complexes with the best tanning properties. With tartaric acid, it is shown that one gram-mole of this acid for every two gram-moles of iron gives the optimum tannage, a shrink temperature of 93°C and a minimum of swelling. However, this point does not coincide with the maximum iron take-up and the reason therefor is sug-

gested. Phthalic acid gives much better results than tartaric but difficulty is encountered in its use due to its low solubility. It was only found possible to incorporate sufficient phthalic acid by first stabilizing the iron sulfate with sodium phosphate and so raising the basicity to at least 20° Sch. For such a tanning liquor, one must use (1) a low concentration of phosphoric acid, just sufficient to stabilize the iron salt (e.g., 0.2 mole per 2 mole Fe). (3) As strong a concentration of phthalic acid as possible; while its low solubility does not permit of solutions stronger than about 0.3 moles per 2 Fe, one can add an excess which will dissolve as the reaction proceeds. It is best to start with solutions of low basicity and to complete the tannage in solutions of as great a basicity as possible. Methods are given of producing concentrated solutions of ferric sulfate, starting with either crude ferric sulfate or with ferrous sulfate and directions are given for practical tannages for sole, calf and kid leathers. It is stated that the sole leather produced is very thin, low-yielding and its water resistance leaves something to be desired—though this could be overcome by impregnating the leather. Its resistance to wear is, however, superior to that of ordinary vegetable tanned leather. By giving the hide two successive tannages with iron, followed by retannage with a synthetic tannin, a more normal sole leather can be obtained. Box-calf and other upper leathers differ in that they require a formaldehyde pretannage and do not require the retannage with syntan. A. N. K.

On the Formation of Complex Ions in Solutions of Alumina and of Chrome Alum. By F. Grall. *Premier Congres International. Union Int. des Socs de Chim. des Ind. du Cuir*, pg. 146, Sept. 1949. Comparative studies were made of the effects of (1) Temperature, (2) Basicification, (3) Additions of neutral salts (NaCl and K_2SO_4), (4) Additions of organic salts (formate and oxalate), on the formation of complexes in solutions of aluminum sulfate and of chrome alum, using the ion-exchange technique. (1) *Effect of Temperature.* M/50 solutions of Cr alum were prepared (1) in the cold (violet); (2) by heating (1) slowly until it became a clear green color (about 65°C); (3) by heating (1) to the boiling point and immediately cooling; (4) by heating (1) and holding at the boil for 15 minutes, then re-cooling. The results indicate that the transformation from violet to green is due to the formation of cathodic acid and non-charged complexes. No anodic complexes were observed. Heating of aluminum sulfate solutions to the boil gave no indication of complex formation. (2) *Effect of Basicification.* Violet chrome alum liquors, brought to 33° Sch., contain a small quantity of acid complexes, whereas basicification of the green solutions results in particle replacement of sulfate groups by hydroxo groups. With M/10 solutions of alum sulfate and basicities of 8, 16, 24 and 38° Sch., no formation of sulfate-complexes was observed. (3) (a) *Addition of NaCl.* On violet solutions of Cr. alum, the non-charged complexes increased in proportion to the added salt and the acidity of both the non-charged and cathodic complexes increased similarly. On green solutions, the acidity of the cathodic complexes decreases with increasing salt addition and it is supposed that chloride is displacing sulfate and that the hydroxo-chloro-chromic cations are unstable. With solutions of alum sulfate, acid-complexes were only observed when the concentration of chloride exceeded 5 NaCl per 1 Al_2O_3 and this only in solutions of less than 33° Sch. (b) *Addition of K_2SO_4.* On both violet and green chrome solutions, addition of K_2SO_4 increases the proportion of uncharged complexes, and their acidity increases with the concentration of sulfate: the sulfate groups displacing hydroxo groups. On solutions of alum sulfate, K_2SO_4 produced acid-complexes only in basic solutions. With M/20 alum sulfate solution, made 3M/20 in K_2SO_4, cathodic complexes were formed containing 1 sulfate group per 2 atoms alum. (4) *Addition of Organic Salts.* In the case of the chrome alum solutions, tanning experiments were made using hide shavings and tanning for 24 hours by shaking all day and allowing to stand overnight. The following checks were run: (1) Swelling Index by the

Method of Meunier & Chambard, (2) Cr_2O_3 in the ash, (3) acid absorbed, by the method of Riess & Papayannis as modified by Theis & Meerbott and (4) the resistance to hydrolysis (W.B.) by the method of Fahrion modified by the Lyons Research Institute. (a) *Formate.* On chrome alum solutions, the results indicate that increasing additions of formate gives (1) decreasing cathodic complexes and a reduction in the Cr_2O_3 absorbed by the pelt (2) a reduction in complex-bound sulfate and of H_2SO_4 absorbed by the pelt with corresponding increases in formato-complexes and of HCOOH absorbed; the displacement of sulfate by formate groups being almost quantitative, (3) the resistance to hydrolysis (W.B.) increases, the effect being marked for even small additions of formate, and it is noticed that (W.B.) is not a function of the quantity of Cr_2O_3 absorbed. Alum sulfate solutions of 0° an 33° Sch., treated with amount of formate or formic acid varying from 0 to 6 moles per 1 Al_2O_3, gave no indication of the formation of formato-complexes. (b) *Oxalate.* On Cr. alum solutions of 33° Sch., (1) the quantity of cathodic chrome falls rapidly with increasing addition of oxalate; (2) at 2 moles oxalate per 1 Cr_2O_3, the chrome is entirely present as uncharged oxalato-complexes and at 6 moles oxalate it is entirely present as anionic oxalato-complexes. The tanning tests show: (1) Swelling falls to a minimum at between 2 and 3 moles oxalate and then increases; (2) the Cr_2O_3 fixed decreases slowly as the uncharged complexes increase (up to 2 moles oxalate per 1 Cr_2O_3) and then falls rapidly until, at 6 moles oxalate, the solution is no longer capable of tanning; (3) the leather only contains sulfate ions when the liquor contains complex-bound sulfate (up to 2 moles oxalate); (4) W.B. increases with increasing oxalate addition as long as no anodic complexes are present (up to 2 moles oxalate) and then decreases rapidly; (5) the shrink temperature (determined on pieces of pelt tanned in the same manner as the shavings) remains above 100° up to 2 moles oxalate and then falls. With M/25 alum sulfate, with oxalate varied from 0 to 8 moles per 1 Al_2O_3, no complex formation was found in O basic solutions. With solutions of 33° Sch., flocculation occurred when oxalate was equal to or less than 2 moles per 1 Al_2O_3, but higher amounts gave cathodic complexes in which sulfato and oxalato groups coexisted. Thus, at 8 moles oxalate, a complex was obtained containing 1 sulfato group and 2 oxalato groups. In no case were uncharged or anodic complexes observed. From the data the following conclusions were drawn: (1) The existence of alum compounds, analagous to the green chrome salts produced by heating the solutions, seems improbable. (2) In chrome solutions, basicification modifies the structure of the complex ions; sulfato groups can displace hydroxo groups. (3) Addition of neutral chlorides and sulfates to chrome solutions modifies the complex due to penetration of chloride and sulfate groups into the complex, the sulfates being the more effective. However, this difference in power of penetration does not seem to account for the differences in pH which they produce in chrome solutions. This addition of neutral salts is of less importance with alum sulfate solutions than with chrome, resulting in an increase in the quantity of oxide fixed by pelt in the case of the former and a decrease in the latter; in alum solutions, cathodic complexes are produced which have greater tanning power than the simple cations whereas, in chrome solutions, the quantity of uncharged complexes is increased and these fix with difficulty. (4) Additions of formate and oxalate increase the uncharged and anionic complexes in chrome solutions whereas, in alum solutions oxalates (only) increase the cathodic complexes. From the above, it is deduced that chromium has much greater powers of forming complexes than has aluminum and that it is this difference which accounts for the differences in the stability of the tannage produced. In the case of chrome tannage the observation that resistance to hydrolysis is not related to the fixed Cr_2O_3 and the important part played by the anions present, are stressed. A. N. K.

"Studies on the Formation of Complexes in Concentrated Solutions of Basic Sulfates and Chlorides by Means of Ion-Exchange and Spectrophotometric Methods,

and Their Action on Collagen." By K. H. Gustavson. *Premier Congres International. Union Int. des Socs. de Chim. des Ind. du Cuir*, pg. 21, Sept. 25, 1949. Spectrophotometric and ion-exchange studies on diluted and concentrated solutions of basic chrome chlorides and sulfates, both in the presence and absence of their sodium salts, give specific data on their composition and structure. Dilute solutions of chemically pure chrome chloride of acidity 67 (0.4 eq/litre of Cr) contain only cationic chrome complexes, and even in concentrated solutions (8eq/litre of Cr) practically all the chrome is in this state and does not contain complex-bound Cl groups, but only hydroxo- or oxo-chrome complexes. This also holds for similarly dilute solutions containing sodium chloride (to give a composition corresponding to $Cr_2(OH)_2Cl_4 \cdot 2\ NaCl$). In very concentrated solutions, only a small percentage of the total chrome is in the form of non-charged complexes, the major part being in the form of cationic complexes. Some of these are in the form of chlor-hydroxo cations. The absorption spectra of diluted and concentrated solutions of the chlorides, measured at a concentration of 0.06 eq/litre of Cr, show marked differences, the optical density of the concentrated solution being much greater than that of the diluted solution measured at the same concentration. Further, the maximum absorption of the concentrated solutions is displaced toward the longer wave lengths. In dilute solutions of chrome sulfate of acidity 67, free from Na_2SO_4, all the complexes are positively charged, with one SO_4'' held by two atoms of chrome. In the concentrated solutions (8 eq/litre of Cr) about 90 per cent of the total chrome is present as cations, the remainder being uncharged. On addition of one mole of Na_2SO_4 per mole Cr_2O_3 (giving a composition corresponding to $Cr_2(OH)_2(SO_4)_2\ Na_2SO_4$), the ion-exchange method indicates that practically all the chrome carries a positive charge in the dilute solutions, whereas the principal constituents in the concentrated solutions are uncharged complexes. A few per cent of the total quantity of chrome is in the form of negatively charged complexes, the rest having a positive charge. The extinction coefficient of the concentrated solution is higher than that of the dilute solution, measured at the same concentration. Spectrophotometric results, on the effect of neutral sulfates on the structure of the basic chrome sulfate complexes, confirm those obtained by the ion-exchange method. Tannage of skin for a short time (2-4 hours) with sulfate of acidity 67 ($Cr_2(OH)_2(SO_4)$) in aged solutions and in solutions diluted immediately before use showed that the skin fixed 50-100 per cent more chrome from the freshly prepared solutions (containing mainly uncharged complexes) than from aged solutions (containing mainly cationic complexes). The shrink temperature of hide tanned in the former solution was several degrees lower than that of hide from the aged solutions. Skin tanned in basic sulfate solutions free from sodium sulfate gave the same fixation of Cr and same shrink temperature whether the solutions were aged or freshly prepared. Basic chrome chlorides behave the same independently of the concentration or of the presence or absence of NaCl. Difference in the behavior of the usual basic chrome sulfate liquors, depending on their chrome content, is supposedly due to the fixation of unchanged Cr complexes. The results of these studies are in agreement with that conception of chrome tannage which regards it as a multiple binding of positively charged Cr complexes with the negatively charged carboxyls of the hide, leading immediately to a direct association between the carboxyls with the Cr atom of the complex by a change from the labile electrovalent linkage to a stable coordinate covalent linkage. A supplementary fixation of non-cationic chrome complexes on the unionized groups of the collagen under certain circumstances is shown. A. N. K.

The Effect of Acids and Salts on the Tannery Properties of the Catechol Tans. By H. W. Humphreys and J. H. Atkinson. *Premier Congres International. Union Int. des Socs. de Chim. des Ind. due Cuir.*, pg. 82, Sept. 1949. The sole leather tanner has long known that the degree of acidity and the quantity of non-tans in the liquors are important in deter-

mining type and characteristics of the leather produced. Certain materials are well-known for their ability to produce acid while others are used for the mellowing effect of their non-tans, and the tanner has balanced these. The non-tans can be divided into organic and inorganic, the latter being frequently called "salts". In 1940, the English tanner was cut off from his supply of pyrogallol materials and was forced to produce sole leather from blends of quebracho and mimosa together with a small proportion of myrabs. Fortunately, the extract manufacturers and some leather chemists had studied the possibility of using catechol tannins as replacements for the pyrogallols. Okell *(la Bourse aux Cuirs Belique* 1947, **11**, 17) gives a very detailed report on the latest British practice in this respect. While being largely in agreement with Okell's point of view, the authors feel that he, and others, have not accorded proper importance to the part played by the salts. The acidity and salt content and their effects on the leather are actually two related problems which require separate study. Certain basic ideas being established for each, one should study the effects of the variation of these two factors in the same liquor. For some years, it has been known that addition of acid to the liquors, especially to those high in catechol tans, produces a firmer leather but it has not been clearly established as to whether this is merely the effect of pH or not. If it were merely a matter of pH, one would expect the same result regardless of the acid used. However, it was soon realized that the matter was not so simple and that other factors, perhaps the quantity of acid present, were of basic importance. Two sets of tanning tests were made, (using pieces of hide partially delimed with sodium bisulfite), using sulfited quebracho at pH's of 5, 4 and 3; in the one test, sulfuric acid was used to adjust the pH while formic acid was used in the other. With sulfuric acid, after 4 or 5 days tannage, the leather tanned at pH 3 was much firmer than that at pH 5 but, as tannage proceeded, the difference became less marked and, at the end of the tannage (33 days), those tanned at pH 3 were only slightly firmer than the others. With formic acid, on the other hand, the initial firmness persisted and increased as the leather passed through the stronger liquors. The authors feel that the difference in firmness was due to the greater quantity of acid present when formic is used and that it is not sufficient merely to lower the pH but that the liquors must contain appreciable quantities of acid. Another test was made to simulate hot-pitting. Here the leather is held in liquor of pH 3.0 - 3.3 for several days. In the test, sulfited quebracho of 18° Be′ and pH 3.2 was used, the acidity being adjusted with (1) Sulfuric, (2) Formic, (3) Lactic, (4) Acetic acids, respectively, and leather suspended therein, for 7 days @ 40°C. Both out of the liquors and after drying and finishing (but not rolled), the firmness increased in that order. Analysis showed that firmness paralleled the acid content of the liquors.

	(1) Sulfuric	(2) Formic	(3) Lactic	(4) Acetic
pH	3.34	3.30	3.33	3.33
Acid content, milligram equiv.	93	195	203	1260
Salts, milligram equiv.	327	342	334	292

Another test was made using a similar set of hot-pits and the same 4 acids. For this, the quantity of sulfuric acid (in milligram equivs.) necessary to bring the pH to 3.3 was determined and the same quantity (mg. equivs.) of each of the other acids was used in their respective liquor. As might be expected, the pH values, so obtained, varied considerably: sulfuric—3.3; formic—3.8; lactic—4.16; acetic—4.4. The leathers remained in the liquors for 7 days at 40°C as before. At the end of the tannage, there was no appreciable difference in the firmness of the leathers, despite the great pH differences. Hence, for firm leather, it seems that it is not sufficient merely to hot-pit at a low pH but that a good reserve of

organic acid must be present. It is suggested that 1 per cent or 1.5 per cent (on the dry weight of the extract, if mimosa is used alone) of either formic or lactic acid would be satisfactory. If formic is not available, one can use 2 per cent acetic (which will bring the pH to about 3.85) and then lower to 3.2 - 3.3 with 0.5 per cent sulfuric (on the dry weight of the extract). Having obtained a clearer view of the effects of acidification, it was felt desirable to study the effect of salts in a similar manner. Other factors remaining constant, an increase in the salt content gives softer leather but this depends on the type of salt present and the effect can be varied by varying the acidity of the liquor. The estimation of the salts is based on the titration curve, the ash and sulfated-ash content and on the alkalinity of the ash. More recently, the salts have been estimated by the resin-exchange method of Cheshire but, while this method gives good results in the case of catechol tans, it seems to fall down on the pyrogallols, Atkin and Burton have studied this question and have recently published [(*J.S.L.T.C.* **33,** 52 (1949)] a method, which seems to be satisfactory for differentiating between the salts of strong acids and those of weak acids. Briefly their procedure is as follows: the natural acidity of the liquor can be determined by titration to pH 5.8 with alkali; the buffer salts (salts of weak acids) can be determined by titrating the liquor to pH - 2.0 with N/2 acid. The sulfated ash gives total salts and the difference is the content of salts of strong acids. Using the above technique, the effect of varying the concentration of neutral salt was studied using sodium sulfate and mimosa liquor. Four sets of liquors were used: the first containing no added salt except that naturally present; the other three contained increasing quantities of sodium sulfate. The pH was adjusted with H_2SO_4. The acid and salt content were as follows:

Liquor	(1)	(2)	(3)	(4)
Be′	0.7	2.7	4.7	8.7
pH (H_2SO_4)	3.66	3.7	3.7	3.72
Acid	10	7	6	6
Salt	49	237	444	857

To simulate practical conditions, the stock was surface-delimed ($NaHSO_3$) and tannage started at the above pH value and the pH gradually lowered to 3.1 using sulfuric acid. The tannage lasted 36 days and the salt and acid contents of the head liquors in which the stock was hot-pitted were as follows:

Liquor	(1)	(2)	(3)	(4)
Be′	17	18.5	19.8	21.8
pH (H_2SO_4)	3.21	3.23	3.27	3.24
Acid	116	113	103	101
Salt	120	356	565	987

During the whole tannage at room temperature, there was practically no difference in the firmness of the leathers from the different liquors, but in the warm liquors the differences were very marked. After 24 hours in the warm liquors, the leather in the liquors to which the salt had been added, became progressively softer while that in the acidified mimosa without salt became excessively firm. No difference could be seen in the rate of penetration. After finishing, there was practically no difference in the firmness of the pieces tanned in liquors 1, 2, 3, but there was a distinct loss of firmness in that from 4 and the leather was much less plumped than the others. It seems, then, that the addition of sodium sulfate up to 1,000 mg. equiv. per liter in the cold liquors does not have much effect on the firmness

at this stage but that such additions to the hot liquors gives a lessened firmness in the wet which is rather less evident in the finished leather. Another experiment was made using a stock mimosa liquor which @ 19° Be′ contained 500-600 mg. equiv. of added sodium sulfate. One set was run at the natural pH of mimosa (4.6); a second was acidified to pH 3.2 with sulfuric; a third was acidified to pH 3.2 with formic acid:

Be′	Approx. Salt Content	Mimosa Natural		Acidified with Sulfuric		Acidified with Formic	
		Acid	pH	Acid	pH	Acid	pH
7	410/430	15	5.	38	3.2	280	3.2
13	530/580	20	4.6	45	3.2	250	3.2
19	600/620	25	4.6	65	3.2	205	3.2

During tannage, there was no visible difference in firmness between the pieces tanned at the natural pH and those from liquors acidified with sulfuric, but those tanned with formic were much firmer. To study the effect of the type of salt, the 5 mimosa tannages were run:
(1) Mimosa, natural pH (4.6); 19° Be′; no added salt.
(2) Same as (1) but 500 mg. equiv./l sodium acetate added.
(3) Same as (2) but acidified to pH 3.2 (H_2SO_4).
(4) Same as (1) but 500 mg. equiv./l sodium sulfate added.
(5) Same as (4) but acidified to pH 3.2 (H_2SO_4).
Their salt/acid characteristics were:

°Be′	(1)		(2)		(3)		(4)		(5)	
	Acid	Salt	Acid	Salt	Acid	Salt	Acid	Salt	Acid	Salt
7	13	95	73	233	413	220	13	280	95	285
13	25	90	135	373	390	380	15	403	105	388
19	38	127	190	484	458	499	30	512	80	504

Throughout the tannage, the leather from No. 3 was much firmer than any of the others while that from No. 5 seemed a trifle less firm than that from No. 1. While one cannot yet establish definite rules as to maximum salt contents for firm leather, one must differentiate between the effects of salts of strong and those of weak acids on the firmness of the leather. With liquors predominantly catechol, it is the quantity of acid present which is important and the tanner should select his acid with care. A. N. K.

Preparation, Constitution and Tanning Action of Synthetic Tannins. F. Stather, R. Schubert and R. Bellman. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 5, 3 (1950). The literature on syntans is reviewed (77 references). Little systematic work has been published to show how the tanning properties of sulfoaromatic compounds are influenced by the structure of the starting compound, the degree and method of sulfonation, and conditions of condensation. Presumably this work has been done by manufacturers of syntans, but publication has been limited mostly to patentable discoveries. The authors report the results of over 700 experiments, in which 18 different starting compounds were each sulfonated under three different conditions, and then condensed (alone or in combination with another sulfonate or an unsulfonated compound) with HCHO in varying amounts, either under acid or alkaline conditions. All the products were adjusted to pH 3.5, analyzed for apparent tannin content by the hide powder method, and tested for gelatin precipitation and precipi-

tability by NaCl. When significant amounts of tannin were found, tanning tests were made with dehaired, delimed calf skin, and tan values and combining values [This *Journal* **47**, 629 (1952)] were measured. The starting materials were: (1) aromatic hydrocarbons (benzene, toluene, xylene, naphthalene); (2) monophenols (phenol, cresol, xylenol, 1- and 2-naphthol, 0-cresol, and commercial mixed cresols); (3) polyphenols (commercial catechol and resorcinol); (4) nitrogen compounds (nitrobenzene, dinitrophenol, aniline); (5) chlorine compounds (a mixture of chlorinated phenol, cresol, and xylenol); and (6) a purified lignosulfonic acid from spruce. Three sulfonation processes were employed—with 1 mol H_2SO_4 at 90-100°C., with 2 mols at 110-120°, and with one mol at 150-160° to obtain sulfones. Condensation was done with 0.5 to 4 mols HCHO, generally at 90-100°. The apparent tannin content of the uncondensed sulfonates of the hydrocarbons, monohydroxy-monocyclic phenols and nitro-compouds was very low, but that of the dihydroxy phenols, naphthols, aniline, and the chlorophenols was appreciable. For any starting compound, the apparent tannin content generally was highest for the sulfonemonosulfonic acid, and lowest for the disulfonic acid. Tanning tests showed that only the naphthol sulfonates had any real leather-forming properties. The best was bis(hydroxynaphthyl) sulfone monosulfonate, which produced a leather with degree of tannage 67. With regard to the tanning properties of the HCHO condensation products, the following general conclusions were drawn. (1) The degree of sulfonation should be just enough to impart adequate solubility; this varies with the starting compound and the material with which the sulfonate is condensed. (2) Better products result from condensing a strongly sulfonated compound with an unsulfonated phenolic compound than from condensing two moderately sulfonated molecules. (3) Tanning power depends on both the number and location of phenolic OH groups, and is enhanced when the compound contains at least one, preferably two, phenolic rings bearing no sulfonic groups. This does not hold for catechol derivatives. (4) Condensation in acid media generally, but not always, yields, better results, because over-condensation is likely in alkaline medium. The quantity of HCHO must be sufficient to avoid the presence of uncondensed unsulfonated compounds, but use of too much HCHO, or condensation at too high a temperature, leads to formation of large aggregates that penetrate poorly into hide fibers. (5) Tanning power is better for derivatives of polycyclic than for monocyclic phenols, for derivatives of 2-naphthol than for 1-naphthol, and for polyphenols than for monophenols. When unsulfonated, monocyclic phenols are condensed with a sulfonated phenol, tanning power decreases in the order phenol, cresol, xylenol, but sulfonated cresol gives better products than sulfonated phenol. (6) Lignosulfonic acid, alone or mixed with other sulfonated compounds, gives products of good tanning power when condensed with unsulfonated phenols. Addition of lignosulfonic acid to alkaline condensation products sometimes improves their tanning power, partly by improving their solubility. (7) Tanning power increases with molecular size to a certain maximum, and thereafter declines. The molecular size of any product depends on the molecular weight and degree of sulfonation of the starting material, the kind and amount of unsulfonated compounds therewith condensed, the quantity of HCHO, and the conditions of condensation. (8) In evaluating syntans, a tanning experiment is the only conclusive test. The tannin determination merely eliminates materials of too low purity (below 60) to be valuable. Tan value and combining value should be at least 50 and 30 respectively. The fraction precipitated by saturated NaCl generally should be 60-70 per cent for usable replacement syntans. On the basis of these experiments, usable replacement syntans can be made by HCHO condensation (under acid A) or alkaline (B) conditions as indicated), of the following: 1. Cresol sulfonic acid with itself or with 2-naphthol (A). 2. Sulfonated catechol with itself (A or B), or with unsulfonated catechol (A). 3. 1-naphthol sulfonic acid with 2-naphthol or with dihydroxydiphenylsulfone (B). 4. 2-naphthol sulfonic acid with phenol, cresol or 2-naphthol (A), or with dihydroxydiphenylsulfone (B). 5. Dihydroxydiphenylsulfone sulfonic acid with phenol (A). 6. Lig-

nosulfonic acid with phenol or cresol (A), and with dihydroxydiphenylsulfone (B). 7. Lignosulfonic acid plus phenolsulfonic acid with dihydroxydiphenylsulfone (B). 8. Lignosulfonic acid plus cresolsulfonic acid with cresol or phenol (A or B), and with cresolsulfonic acid or 2-naphthol (B). 9. Lignosulfonic acid with sulfonated catechol (B), or with sulfonated and unsulfonated catechol (A). 10. Lignosulfonic acid plus 1- or 2-naphthol sulfonic acid with phenol or cresol (A). 11. Lignosulfonic acid plus sulfonated 2-naphthol with 2-n-aphthol (B). H. B. M.

The Influence of Different Condensing Materials on the Tanning Action of Condensed Phenolic Synthetic Tanning Materials. F. Stather and H. Nebe. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 7, 34 (1951). Although the use of aldehydes and ketones other than HCHO, for condensing sulfonated phenols to form syntans, has been described (mostly in patents), data on comparative tests with different condensing agents is almost wholly lacking. Mixtures of 2 mols phenol and 1 mol 2-naphthol, sulfonated with from 2 to 6 mols H_2SO_4, were condensed with 2 mols of 10 different aldehydes or ketones. The ratio of sulfonic groups to aromatic molecules varied from 2:3 to 6:3. The molecular ratio of phenolic compounds to condensing agent was always 3:2; therefore the products were assumed to contain mostly trinuclear polymers, although all the products doubtless were heterogenous. Sulfonation was done at 140°C., and condensation at 60 to 110° depending on the condensing agent. The products were analyzed for apparent tannin content at pH 3.5, and tanning tests were made. The resulting leathers were graded numerically from 1 to 5, from very good tanning action, producing a full, soft, non-brittle leather, down to no recognizable tanning action. With HCHO, grade 1 leathers were obtained with products sulfonated with 2 - 2.8 mols H_2SO_4, all attached to the 2-naphthol nucleus. These products had analytical purities of 75, and the leathers shrank at 78-83°C. The leather character always, and the analytical purity generally, declined with increasing degree of sulfonation. Equally good leathers were obtained with products condensed with acetaldehyde, paraldehyde, and acetone, but these products required a higher degree of sulfonation to secure adequate solubility, a minimum of 3 mols H_2SO_4 for 3 mols of phenolics for acetaldehyde and paraldehyde, and 4 mols for acetone. The shrinkage temperatures of the best leathers produced from acetaldehyde condensation products were 68-71°C., and from acetone condensation products 59-60°. The analytical purity was about 60 for the best acetaldehyde products and under 50 for the best acetone products. Condensation products of crotonaldehyde, aldol, acrolein, benzaldehyde, furfural, and acetophenol required still higher sulfonation for adequate solubility. All showed fairly high analytical purities and some leathering action, but produced no satisfactory leathers. However, a good leather was obtained with a phenol-benzaldehyde condensation product, sulfonated *after* condensation. The importance of the presence of one or more phenolic rings devoid of sulfonic group was confirmed. H. B. M.

Investigation on the Dressing and Up-Grading of Furs. I. Microscopic Anatomy of Several Domestic (German) Fur Skins. Fritz Stather. *Ges. Abhandl. deut. Lederinsts. Freiberg/Sa.* No. 4, 3 (1950). Photomicrographs are shown of skins of rabbit, cat, fox, hamster, squirrel, muskrat, martin, skunk, mole, and badger. In contrast to skins used for leather the corium is very thin, and there is no distinction between the papillary layer and the reticular layer. The collagen fibers are thin, uniform, and almost exclusively horizontal. The hair bulbs extend more than half way through the skin. Four to 30 hairs grow from one follicle. In several species, especially rabbit, there is a strongly developed muscle layer just below the skin. *II. Influence of the Most Important Fur Dressing Procedures on the Properties of Fur Leather.* F. Stather, H. Herfeld and K. Sohre. *ibid.* No. 4, 17 (1950).

No chemical-technological process is so completely empirical as fur dressing. Comparative scientific studies of the simplest fundamentals of individual processes are completely lacking. Altho fur dressing resembles leather manufacture in that the skin must be rendered imputrescible and water-resistant, the processes differ, aside from retention of hair and epidermis, because the properties desired in fur skins are quite different from those sought in leather. Furs must be thin, soft, stretchy, flexible, and light; a leathery character is not wanted. Nevertheless a real tannage must be given if the furs are to have adequate strength and aging qualities. The standards of the German Leather Institute have long required, for furs: (1) shrink temperature 75°C. (minimum); not over 5 per cent loss in area at 70°C.; (2) no loss in area, softness or flexibility after washing six times with sodium oleate or Gardinol; (3) 4 to 10 per cent fat (petroleum ether extract); (4) not over 8 per cent inorganic matter other than Al_2O_3 and Cr_2O_3, and not over 8 per cent water solubles; (5) pH value (water extract), 3.5 - 7.0; if below 4.5, then difference number 70 (minimum); (6) tensile strength at least 100 kg./cm.^{2}, stitch tear at least 25 kg./cm., slit tear at least 10 kg./cm., per cent stretch at break, at least 35 per cent; (7) water uptake, from flesh, not over 3 g. and 6 g. per 100 cm.^{2} in 15 min. and 2 hours respectively; (8) air transmittance coefficient at least 800, after clipping (not shaving) the hair; (9) freedom from all skin irritants (soluble Cr compounds, sulfur, amines, diamines, aminophenol, etc.). Experiments were performed to see which of the fur dressing processes in common use were capable of giving a product meeting these standards. Each test was made with 10 rabbit skins, picked out for uniformity. Each lot was soaked two days in water plus Pekorol L, fleshed, rinsed, centrifuged, and treated by one of 24 different procedures, involving different combinations of acid pickle, enzyme pickle, and tannages with formaldehyde, alum, proprietary aluminum compounds (Blankorols), chrome, or syntans. Following tannage the skins were painted on the flesh with a mixture of sulfated train oil, sulfated castor oil and Avirol GB, with or without ammonia depending on previous neutralization, and given the usual mechanical treatments. Use of a strong acid pickle, or an "enzyme pickle" (Oropon E + formic acid + salt) is essential for obtaining satisfactory softness, flexibility and stretchiness. Skins that were merely pickled ("Leipziger process") were superior in these respects, but these had poor stability towards water, and showed marked loss of strength on aging. Skins neutralized after pickling were nearly as good in subjective quality, and showed no loss of strength on aging, but had no stability to washing. Satisfactory subjective qualities together with adequate strength, stability on aging, stability on washing, and shrink temperature, were attained by tanning with HCHO, HCHO + alum, or a commercial Cr tanning compound, but not with alum alone or with the syntans. *III. Investigations on the Formaldehyde Dressing of Fur Skins.* H. Herfeld and K Sohre. *ibid.* No. 5, 78 (1950). This paper deals with amount of HCHO that must be fixed by skins to obtain satisfactory shrink temperature, the conditions for obtaining such fixation, and the reversal of HCHO tannage by displacement of HCHO in acid media. Lots of 5 rabbit skins, previously bated with Creaton 202 + salt, were tanned with 2 to 8 volume per cent of 30 per cent HCHO on the centrifuged weight of the skins., along with varying amounts of Na_2CO_3. After tanning, the skins were brought to pH values varying from 8.4 to 4.4 by treatment with $(NH_4)_2SO_4$, acetic acid + NaCl, or by an alum retan. The finished skins were analyzed and tested for shrink temperature, per cent area loss at 70°C., washability, and water uptake. Formaldehyde content of the skin (by the method of Highberger and Retzsch, *This Journal* **33**, 341 (1938) increased with amount given and decreased with final pH value. Shrink temperature varied from 84°C. (0.65 per cent HCHO) to 65° (0.05 per cent HCHO). Shrink temperature was 74° or higher for skins containing 0.18 per cent HCHO or more. The pH values of such leathers were 6.4 or higher. The per cent HCHO in the hair varied from 50 to 100 per cent of per cent HCHO in clipped skin (see Theis, *Chem. Abstracts* **38**, 4968^6). Data are given on HCHO combined with hide powder after treatment for 1 to 48 hours with 2 to 40

ml. of 30 per cent HCHO per 100 g. hide powder, in the presence of Na_2CO_3 to give a final pH value of 7.5 after 48 hours. Maximum HCHO fixed was 0.66 - 0.68 per cent. This maximum was heached in 48 hours with 10 per cent HCHO, in 1 hour with 20 or 40 per cent HCHO, and not at all with 2 or 5 per cent HCHO. Hide powder tanned to contain 0.41 per cent HCHO was treated with acid (HCl or HCOOH), with and without the presence of salt, (a) before drying, (b) immediately after drying, or (c) after drying and aging six weeks. The undried, HCHO-tanned hide powder lost about 64 per cent of its bound HCHO at pH 2, and about 50 per cent at pH 3.0; dried hide powder lost about 50 per cent, and dried, aged hide powder lost only 27 per cent of its initial HCHO at pH 2, and lesser amounts at pH 3. Loss of HCHO on acid treatment decreased with increasing temperature of drying. Further tanning tests were made in which amount of HCHO, amount of Na_2CO_3 and duration of tannage were varied. All the tests gave adequate shrink temperature resistance to washing, and strength. Best results for character of leather were obtained by tanning 2 days with 1.5 volume per cent HCHO on the centrifuged skin weight, with enough Na_2CO_3 to give a final pH value between 7 and 8. Skins thus processed contained 0.33 per cent HCHO and shrank at 80°C. When more HCHO was fixed, the skins were too leathery and were lacking in stretchability. Good results were obtained by an alum tannage *before* HCHO tannage. Retannage with alum is barred because of HCHO displacement in the acid ilquors. The standards for furs have been amended to permit a maximum pH value of 8, and water uptake of 6 and 8 g. per 100 $cm.^2$ in 15 minutes and 2 hours respectively. *IV. The Different Course of Tanning in Leather Manufacture and Fur Dressing.* F. Stather and K. Sohre. *ibid.* No. 6, 40 (1951). Tannage of fur skins differs from that of leather, not only because of the presence of epidermis and hair, but also because the collagen fibers have not been opened up by liming. To demonstrate the difference, pieces of steer hide that were limed in the regular way, and pieces that were merely soaked, were tanned by the various processes used for fur dressing (Leipzig pickle, and tannages with alum, HCHO, chrome, HCHO and alum, and syntan (Tanigan Extra E), following either the Leipzig pickle or an enzyme pickle. The pieces tanned without unhairing all were harder and stiffer than the limed pieces. Penetration of tanning agent was much slower and took place almost exclusively from the flesh side. Further tests with pieces that were (a) soaked, (b) soaked and defatted, (c) soaked, limed, delimed and bated, and (d) defatted after treating as in (c), showed that removal of fat had very little effect on penetration of chrome, alum, or HCHO. Photomicographs, and data on composition (including layerwise distribution of tanning agent) and physical properties are given. *VII. Investigations on Combined Aluminum-formaldehyde Dressing of Fur Skins.* Hans Herfeld. ibid. No. 7, 21 (1951). Rabbit skins were tanned with alum salts and retanned with HCHO. Variables studied were the quantity of $K_2A_2L(SO_4)_4$, duration of alum tannage, substitution of Blankorol A or Blankorol F for alum, and amount of HCHO used in retanning. There was progressive loss of flexibility and stretchiness, and increase in leathering, as the quantities of either alum or HCHO were increased, and these undesired changes were more marked when tannage was done with the Blankorols. The chief advantage of the alum pretannage was a marked lowering of water absorption compared to skins tanned solely with HCHO. When skins are pretanned with alum, less HCHO should be used than in straight HCHO tannage. The procedure recommended is to pretan pickled skins with 10-20 per cent K alum, 30 per cent NaCl, and 600 per cent H_2O (on centrifuged weight) for 2 days, adjusting the pH value to 4.0 - 4.5. Centrifuge, and retan with 1 per cent (by volume) of 30 per cent HCHO, 20 per cent NaCl, and 600 per cent H_2O, plus 2-3 per cent Na_2CO_3, for 2 days, with a final pH value of 7.0 - 7.5. The K alum can be replaced by 4-6 per cent Blankorol A or 8-12 per cent of Blankorol F, but this has no advantage. H. B. M.

Warble Fly Control in Denmark. By J. S. Aabye. *Das Leder* **3,** 204 (1952). The life cycle of the warble fly is reviewed. The larvae after penetrating the skin, migrate to various locations in the animal. All eventually perish, except those under the hide at the animal's back. Denmark first adopted a dewarbling regulation in 1923. Percentages of warbled hides in 1950 were as follows: South Jutland, 4.47 per cent; North Jutland, 0.92 per cent; Islands, 0.00 per cent. I. D. C.

Semi-micro Method for the Determination of Tan and Combining Values. By W. Grassman and O. Endisch. *Das Leder* **3,** 211 (1952). A semimicro method for determining tannin has been described [*see This Journal*, **47,** 205 (1952)] and a similar method for determining tan and combining values is needed. The following method is proposed: Weigh unchromed hide powder, containing 0.5 grams of dry matter, into a filter bell fitted with a cotton plug and capillary syphon, close with a gauze, then wash the powder by syphoning through it 100 cc. of water in 2-4 hours. Rinse the washed powder into a tared, 50 cc. shake bottle and adjust the weight of contents with water to 13 grams (12.5 grams of water). Prepare 1 per cent and 6 per cent solutions, on the pure tannin basis of the tanning material, as for tannin determination, and centrifuge. Add from a burett 12.5 cc. of the tannin solution in five 2.5 cc. portions at half hour intervals for a 3-hour tannage or at hourly intervals for a 24-hour tannage. Shake at 30-40 r.p.m. After either 3 or 24 hours, pour the hide powder and solution onto a glass filter (No. 1G1). Centrifuge the filtrate and transfer 2 cc. of it and 1 cc. of the original tannin solution to flat-bottomed silver dishes (3 cm. diameter and 2 cm. high), evaporate, and dry to constant weight at 100°C. The difference in weight of the two residues multiplied by 12.5 is the weight of the tannin taken up by 0.5 grams of hide powder and this value multiplied by 200 is the tan value. To determine combining value, rinse all hide powder from the shake bottle to the filter and wash with 100 cc. of water from an overhead reservoir in 8-10 hours. Transfer the washed, tanned material quantitatively to a silver dish, dry first at 40°, then one-half day at 60-80° and finally at 100° to constant weight. This weight minus 0.5 multiplied by 200 is the combining value (tannin fixed by 100 grams of hide powder). I. D. C.

Application of the Karl Fischer Rapid Water Determination Method of Tannery Chemical Work. By J. A. Sagoschen and E. Mantzell. *Das Leder* **3,** 213 (1952). The Karl Fischer method is described. The endpoint should be determined electrometrically, for example by the Dead-Stop-Method of Foulk and Bawden (*Jour. Amer. Chem. Soc.* **48,** 2045 (1926)). The method may be applied to leather or tanning materials as follows: Weigh from 0.5 to 1 gram of the ground material into a titration beaker, add 10 cc. of methanol and cover the beaker. Let stand at room temperature for from 10 minutes to at most an hour, then titrate with the Karl Fischer reagent. It is not necessary to remove the sample from the solution. Coarse, unground material (pieces of leather or bark) can be used, but more time (up to 24 hours) will be required for extraction of the water from the sample by the methyl alcohol. Results by this method, in general, agree well with those by other methods, such as oven drying or xylene distillation. I. D. C.

A Simple Method for the Determination of Water in Leather and Other Substances. By H. Scholz. *Das Leder* **3,** 218 (1952). Determination of moisture in leather by oven drying requires 4-8 hours, or even overnight, preparation of the sample is laborious and may permit moisture changes, other volatile matter is calculated as moisture, and the small amount of sample used (2 grams), may not be representative of the whole. The method is,

therefore, not satisfactory for factory control work. A xylene distillation method has been used for determining water in oils, and is also suitable for leather. A large sample (20 grams) should be used and the leather may be in large pieces. A determination can be made in 10 minutes. I. D. C.

The Analysis of Fatliquors. By A. Panzer and W. Niebuer. *Das Leder* **3,** 219 (1952). The following method is outlined: Weigh 2 grams of oil into a separatory funnel, shake vigorously with 25 cc. of petroleum ether and 25 cc. of 50 per cent alcohol, then let stand (best overnight), until the two layers separate. Transfer the layers to separate, weighed erlenmeyer flasks, distill off the solvent and dry the residue to constant weight. The aqueous-alcohol layer (Fraction A) contains sulfonated material. The ether layer (Fraction B) contains neutral fat with free fatty acids and unsaponifiable matter. If the separation is not satisfactory use ethyl ether and 50 per cent alcohol, doubling the volumes, if necessary. Dissolve Fraction A in hot alcohol and filter from inorganic components. The filtrate can be examined for sulfuric acid esters (SO_3 content) by the Wizoff method and for sulfonic acid esters by the Hintermaier method, which is based on solution of the sulfonic acid in amyl alcohol. Free fatty acids, unsaponifiable and saponifiable can be determined in Fraction B by usual methods. This method has been of practical use in testing all kinds of commercial fatliquors. It, however, can not be used if some of the newer cationic or nonionic emulsifiers are present. I. D. C.

New Spraying and Infra-Red Drying Machine. By A. Meissner. *Das Leder* **3,** 225 (1952). In the machine, which is about 11 meters long, skins move on a belt under the spray, over a heater, then are returned on a second belt above the sprayer. On the second belt the skins pass under a battery of infra-red lamps using 6-10 kilowatts. Surface radiation is 0.43 watts per square centimeter and the temperature only 480°C. I. D. C.

Tanning as a Dehydrating Softening. By A. Brenner. *Oesterreichische Leder-Zeitung* **7,** 242 (1952). Review of an article by F. Seelich in Wiener Klinische-Wochenscrift 60, 709 (1948). The principles of macromolecular chemistry can be applied profitably to tanning theory. I. D. C.

Synthetic Leather Oiling Materials. By Walter Pense. *Oesterreichische Leder-Zeitung* **7,** 263 (1952). Methods for oiling leather are reviewed. During the war suitable substitutes for train oil, tallow and degras were developed and marketed as derminolöl, derminolfett and derminoldegras respectively. Whereas animal oils are lighter than water, derminolol is heavier, so that mixtures can be made having nearly the same specific gravity as water. The oil mixture, therefore, has little tendency to separate from water and more stable emulsions are formed. The synthetic products did not discolor on aging, so were especially good for white leathers. They were also suitable for furs. I. D. C.

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ITALIAN

CHESTNUT EXTRACT

SOLID — POWDER — SPRAY DRIED

MADE FROM LIVE WOOD

TYPICAL A.L.C.A. ANALYSIS

	Solid	Powder	Spray Dried
TANNIN	61.72	66.7	73.5
NON-TANNIN	21.65	21.2	19.1
INSOLUBLES	.65	.6	.7
WATER	15.98	11.5	6.7
ASH	.67	.82	.75

STAINLESS SUMAC CRYSTALS

HIGHEST QUALITY—MADE UNDER THE SUPERVISION OF THE WORLD'S LEADING EXTRACT CHEMISTS

TANEXCO, INC.

549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

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TANEXCO, INC.

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MANGROVE
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STAINLESS SUMAC
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QUEBRACHO
SPECIAL DIPPING EXTRACTS
RAPID TAN "G"

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Manufacturers of the Largest
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